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Effect of Oxidizer Nanostructures on Propulsion Forces Generated by Thermal Ignition of Nano-Aluminum-Based Propellants

Ji Young Ahn[1], Ji Hoon Kim[1], Jong Man Kim[1,2], Deug Woo Lee[1,2], Jong Kweon Park[3], and Soo Hyung Kim[1,2,*]

[1] *Department of Nano Fusion Technology, College of Nanoscience and Nanotechnology, Pusan National University, Busan, 609-735, Republic of Korea*
[2] *Department of Nanomechatronics Engineering, College of Nanoscience and Nanotechnology, Pusan National University, Busan, 609-735, Republic of Korea*
[3] *Nano Convergence and Manufacturing Systems Research Division, Korea Institute of Machinery and Materials, Daejeon, 305-343, Republic of Korea*

We demonstrated that the size and morphology of an oxidizer have strong effects on the propulsion forces of nano-Al-based propellants. Enhanced propulsion forces could be obtained through the creation and addition of various oxidizer nanoparticles and nanowires in nano-Al-based propellants.

Keywords: Al Nanoparticle, CuO Microparticle, CuO Nanoparticle, CuO Nanowire, Propellants, Propulsion Force.

RESEARCH ARTICLE

1. INTRODUCTION

In ancient Korea, multiple fire arrows that each contained a gunpowder pouch and were supported by a cylindrical tube (so-called "Hwacha") were launched in battlefields to repel enemies.[1] Black powder was filled into a gunpowder pouch, which had one capped end and one open end. Upon ignition, rapid burning of the black powder produced hot gas that discharged from the open end of the gunpowder pouch, generating propulsion forces for the arrows. As a replacement for black powder in modern times, energetic materials (EMs) are promising candidates for launching such rocket-propelled arrows. EMs can provide higher energy densities and more powerful propulsion forces than traditional black powder.[2]

EMs have various applications in the modern thermal engineering fields of explosives, propellants, and pyrotechnics.[3] When EMs are ignited by an external energy input, heat and pressure are rapidly generated. This energy output can be controlled by varying parameters such as the size and morphology of the reacting components, the degree of mixing between the fuel and the oxidizer, and pellet density.[4–7] Among the various parameters, the size and morphology of the oxidizer residing in proximity to the fuel component are thought to play a key role in supplying oxygen for effective explosive reactivity of EMs.[8,9] Here, a question arises: can one control the macro-scale propulsion forces generated by EM explosions by simply changing the micro- or nanoscale structure of the oxidizer?

In this study, the effects of oxidizer structures on the propulsion characteristics of thermally ignited EMs used as solid propellants for arrows were examined. Specifically, aluminum nanoparticles (Al NPs) were used as the fuel and CuO microparticles (MPs), nanoparticles (NPs), and nanowires (NWs) were used as the oxidizer for assembling EM composite propellants.

2. EXPERIMENTAL DETAILS

Commercially available, passivated Al NPs (NT base, Inc.) were used as the fuel source. Commercially available CuO MPs (Sigma Aldrich) and NPs (NT base, Inc.) were used as the oxidizer. CuO NWs were fabricated through a combination of electrospinning and calcination processes, which are described in detail elsewhere.[8] EM composite propellants were then fabricated using Al NP and CuO MP/NP/NW powders. Briefly, Al NPs (fuel) were mixed with CuO MPs/NPs/NWs (oxidizer) in an EtOH solution. The mixing ratio between the fuel and the oxidizer was fixed at Al:CuO = 30:70 wt%. The Al/CuO in the EtOH solution was then sonicated under a power of 200 W and

*Author to whom correspondence should be addressed.

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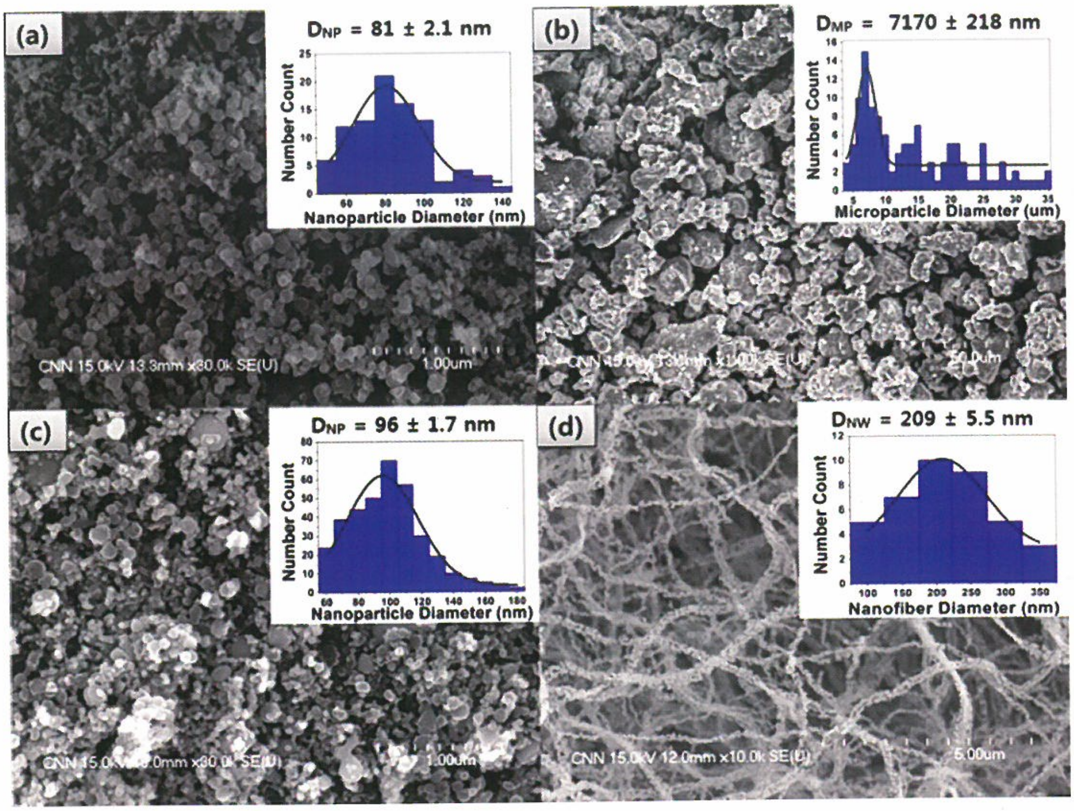

Fig. 1. SEM images of (a) Al NPs, (b) CuO MPs, (c) CuO NPs, and (d) CuO NWs (insets show particle size distributions, and D_{MP}, D_{NP}, and D_{NW} denote the average diameter of MPs, NPs, and NWs, respectively).

frequency of 40 kHz for 5 min to obtain a homogeneous mixture. The EtOH was then evaporated at 80 °C in a convection oven for 30 min.

3. RESULTS AND DISCUSSION

Figure 1 shows scanning electron microscopy (SEM) images of the Al NPs, CuO MPs, CuO NPs, and CuO NWs used in this study that had average diameters of $\sim 81 \pm 2.1$ nm, $\sim 7170 \pm 218$ nm, $\sim 96 \pm 1.7$ nm, and $\sim 209 \pm 5.5$ nm, respectively. After mixing the reacting components, we fabricated three different EM composite propellants composed of Al NPs/CuO MPs, Al NPs/CuO NPs, and Al NPs/CuO NWs.

The mixing ratio of fuel and oxidizer was fixed at Al:CuO = 3:7 wt%. Notably, CuO NWs had highly porous structures that should provide a high interfacial contact area with Al NPs.

The effects of the oxidizer size and morphology on the explosion characteristics of the EM composite propellants were examined by monitoring the flame propagation speed of the ignited EM powders using a high-speed camera (Photron, FASTCAM SA3 120 K) at a frame rate of 30 kHz. Figure 2 shows a series of snapshots of the flame propagation of ignited EM composite propellants. The reaction times of the explosions for the Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite propellants were approximately 5.24, 2.12, and 0.95 ms, respectively. The burn rates of the Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite powders were approximately 5, 34, and 60 m/s, respectively.

This suggests that smaller sizes and larger contact areas of the oxidizer more strongly promoted the exothermic reaction of the EM composite propellants.

Figure 3 shows the pressure traces of the three different EM composites (26 mg samples) ignited by an electrical tungsten wire in a confined cell (~ 13 mL).[8] The maximum pressures increased with Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite powders in ascending order. The maximum pressurization rates of Al NP/CuO NW, Al NP/CuO NP, and Al NP/CuO MP powders were approximately 4.6, 3.2, and 1.1 psi/s, respectively, for the fixed 47% theoretical density (TD). Here, the maximum pressurization rate was determined from the ratio of the maximum pressure to the rise time. The maximum pressurization rate results suggest that the nanostructured oxidizers (CuO NPs and CuO NWs), which have larger specific surface areas than the microstructured oxidizer (CuO MPs), can more extensively interconnect with the surface of the fuel (Al NPs) to generate much higher pressures when ignited.

In order to examine the effect of micro- and nanostructured oxidizers on the macroscale explosion reactivity of EMs, rocket-propelled arrows were fabricated as shown

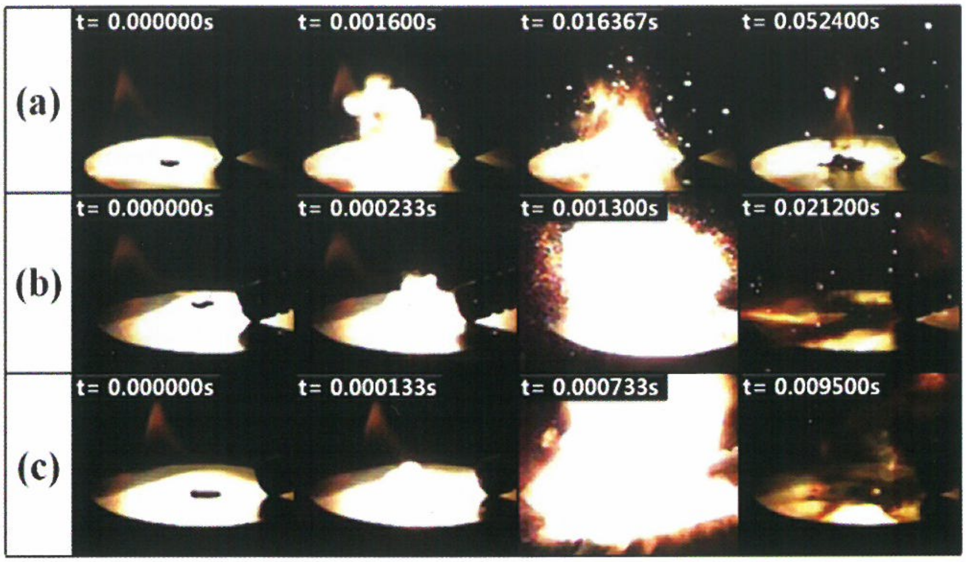

Fig. 2. Snapshots of flame-ignited EM composite propellants (47% theoretical density [TD]) composed of (a) Al NPs/CuO MPs, (b) Al NPs/CuO NPs, and (c) Al NPs/CuO NWs.

in Figure 4. Commercially available carbon-fiber-based arrows (83 cm in length, 1 cm in diameter, total mass of 24 g, Younmoo Archery, Korea) were purchased and are shown in Figure 4(a). The schematic of the custom-made adjustable angle launch pad and snapshots of an EM-propelled arrow guided by the launch pad at a fixed angle of 45° are shown in Figure 4(b). The gunpowder pouch, which was made from a stainless steel tube (inner diameter of 8.5 mm, outer diameter of 13 mm, depth of 50 mm, total mass of 16 g), was filled with 4 g of EM powders, which were then pressed using a wooden peg as shown in Figure 4(c). The resulting pellet density of the EM propellants was calculated to be approximately 47% TD. The propulsion forces of three different EM-based propellants (Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite powders) were compared by launching the prepared rocket-propelled arrows. A fixed amount of EM propellants (4 g) was used to launch all the arrows.

Figure 5 shows a series of snapshots of the launched rocket-propelled arrows and summarizes their measured

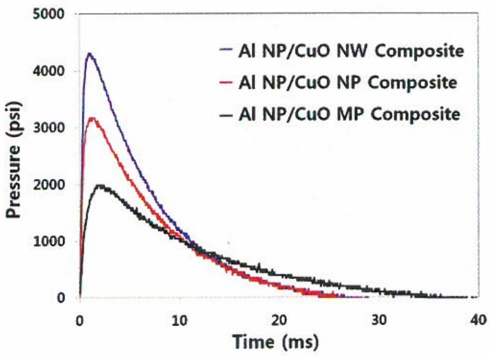

Fig. 3. Pressure traces of various EM composite propellants fixed at 47% TD.

flight distances. From these results, we can first observe a faster burn, brighter flash, and louder explosion at the instance of ignition of the EM propellants with nanostructured oxidizers (Al NPs/CuO NPs and Al NPs/CuO NWs). However, even though a bright flash was seen at the gunpowder pouch for the Al NP/CuO MP composite propellants, the propulsion forces generated were not sufficient to fly the arrows. This suggests that the CuO MPs are less effective than CuO NPs or CuO NWs at providing oxygen to the burning Al NPs.

The resulting flight distances for Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite propellants were found to be $\sim 0.3 \pm 0.1$ m, $\sim 55 \pm 4.0$ m, and $\sim 89 \pm 5.4$ m, respectively. After measuring the resulting flight distance for each launching test, we calculated propulsion forces generated by each EM propellant using simplified Eqs. (1)–(3) as follows:[10]

$$S = U_i t + \frac{1}{2} a t^2 \tag{1}$$

$$U_{ex} = \frac{U_f}{\ln(m_i/m_f)} \tag{2}$$

$$T = U_{ex} \left| \frac{dm}{dt} \right| \tag{3}$$

where S is the flight distance [m], U_i is the initial velocity [m/s], t is the elapsed time [s], a is the acceleration [m/s^2], U_{ex} is the exhaust gas velocity [m/s], U_f is the final velocity ($= U_i$) [m/s], m_i is the initial mass [g], m_f is the final mass [g], T is the propulsion force [N], and dm/dt is the fuel mass change rate.

The theoretically determined propulsion forces for Al NP/CuO MP, Al NP/CuO NP, and Al NP/CuO NW composite propellants were $\sim 0.12 \pm 0.03$ N, $\sim 7.03 \pm 0.27$ N,

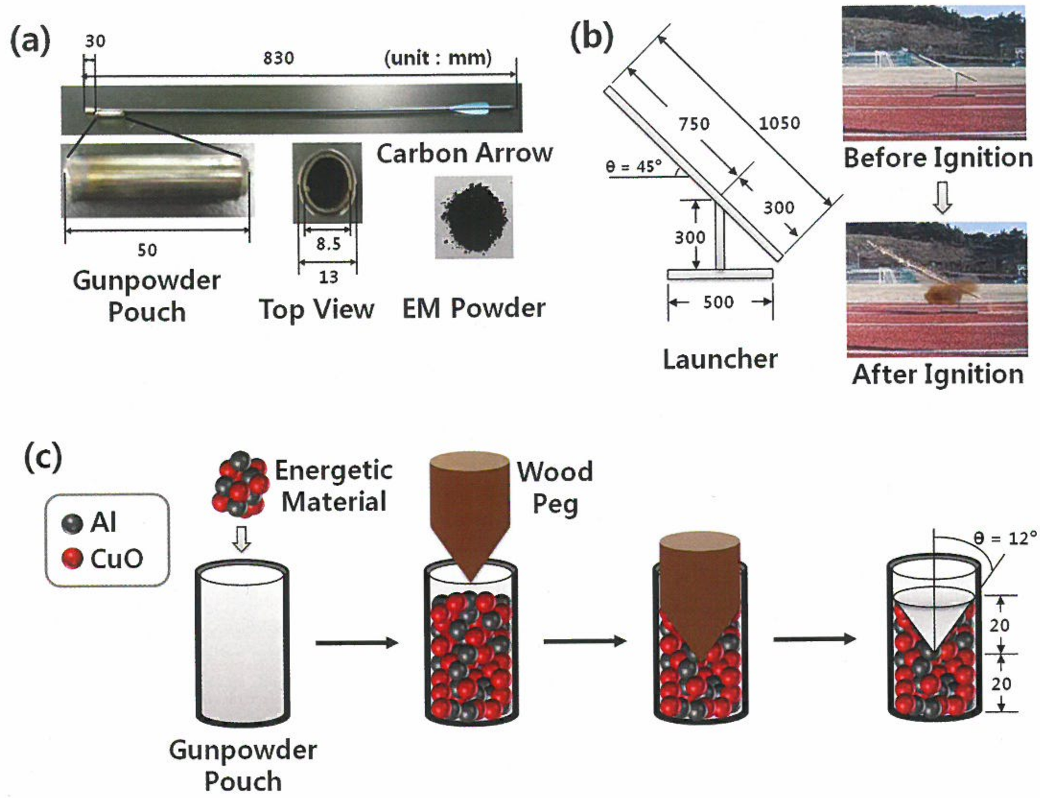

Fig. 4. (a) Pictures of a carbon arrow, gunpowder pouch, and EM powder; (b) schematic of the custom-made launch pad for rocket-propelled arrows and snapshots of an arrow before and after ignition; and (c) schematic of filling a gunpowder pouch with EM composite propellants.

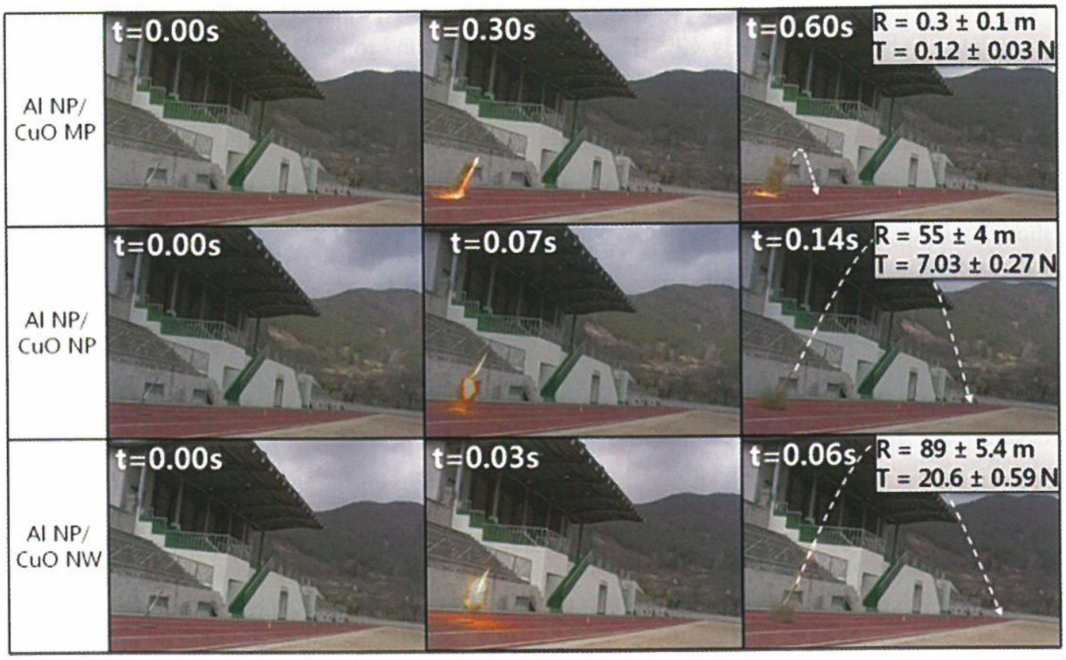

Fig. 5. Snapshots of rocket-propelled arrows containing various EM composite propellants. The measured horizontal flight distances (R) and calculated propulsion forces (T) are shown in the inlays.

and $\sim 20.60 \pm 0.59$ N, respectively. The theoretically determined propulsion forces generated by nanostructured oxidizers in the EM propellants were much larger owing to an effective oxygen supply for burning nano-Al-based EM composite propellants.

4. CONCLUSION

We have demonstrated that the size and morphology of the CuO oxidizer have strong effects on the propulsion forces generated by nano-Al-based propellants. The nanostructured CuO oxidizers significantly increased the resulting propulsion forces of the ignited EM propellants through the rapid supply of oxygen from the oxidizers to the nano-Al fuel. Thus, EM composite propellants with desired propulsion forces can be obtained through the creation of a suitable energetic oxidizer nanostructure.

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