Tuning the ignition and combustion properties of nanoenergetic materials by incorporating with carbon black nanoparticles

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In this study, the effect of carbon black nanoparticle (CB NP) additives on the ignition and combustion properties of Al/CuO NP-based nanoscale energetic materials (nEMs) has been systematically investigated. When an excessive amount of CB NPs (> 1 wt.%) was added to these nEMs, their pressurization and burn rates were considerably suppressed by a magnitude of about 50% due to the heat dissipation and thermochemical intervention in the self-propagating reactions of Al/CuO NPs. The ignition delay time of the studied energetic materials was monotonically reduced with increasing amount of added CB NPs because of the enhancement of their heat transfer properties. The total heat energy generated by the Al/CuO NP-based nEMs gradually decreased with increasing amount of CB NPs because of their thermochemical intervention in the exothermic reaction. Finally, the results of soil explosion testing revealed that the diameter of the produced crater could be controlled by varying the content of CB NPs in the nEM matrix. Therefore, the CB NP additives can be potentially used as a control medium, which affects the heat transfer process and thermochemical interactions between nEM components and is capable of precisely tuning their ignition, combustion, and explosion properties for various thermal engineering applications.

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1. Introduction

Energetic materials (EMs) are composites containing fuel metal and oxidizer components, which are capable of storing chemical energy inherently and then rapidly converting it to thermal energy via external ignition [1–7]. Therefore, EMs are generally used in applications that require high energy conversion in a very short time such as explosives, pyrotechnics, and propellants. Recently, many research groups have investigated nanoscale EMs (nEMs) because their heat energy release rates are much larger than those of macro- and microscale EMs [8–10]. In addition, the thermal and combustion characteristics of nEMs (including thermal decomposition properties, sensitivity, and operational performance [11–15]) can be improved by controlling the size and homogeneous distribution of reacting components.

Controlling the ignition and combustion properties of nEMs is essential for various civil and military applications. Many research groups have attempted to achieve this by adding carbon materials into the EM matrix. Bach et al. [16] developed insensitive nEMs by adding 5 wt.% of graphitized carbon black to Al/WO3-based nEMs; as a result, the modified materials became significantly less sensitive to high magnitudes of mechanical impact and friction while exhibiting high electrostatic sensitivity due to the relatively small content of the carbon modifier. Kappagantula et al. [17] studied the influence of the Al/Teflon-based nEMs impregnated with various carbon nanomaterials (including multiwalled carbon nanotubes (MWCNTs), graphenes, and amorphous carbon nanospheres) on their ignition properties during mechanical impact. They found that the ignition energy of the fabricated nEMs decreased sharply at MWCNT contents below 1 wt.% and then increased slowly at higher MWCNT concentrations. On the other hand, when larger amounts of graphene and amorphous carbon nanospheres were added to the Al/Teflon-based nEMs, their ignition energy gradually decreased. However, it was difficult to quantify the ignition and combustion properties of nEMs by mechanical impaction because of the random formation of localized heating spots on the surface of the modified nEMs.

Carbon materials have been also utilized to improve the thermal properties of various functional composites because of their high thermal conductivity and good light absorption properties [18–24]. Among various carbon materials, carbon blacks (CBs) are frequently used as functional additives since they are relatively inexpensive and can be easily manufactured. Many research groups have used CBs as a light absorber for igniting nEMs by laser beam irradiation [16,23,24]. However, the role of CBs as a heat transfer medium in the nEM matrix ignited by various thermal heat sources...
has not been systematically explored yet. Generally, nEMs containing Al particles as the fuel metal have relatively low thermal conductivity due to the existence of an oxide layer on their surface [25]. In order to enhance the heat transfer properties of Al-based nEMs, the addition of CBs to their matrix can be considered as a potential strategy. Therefore, it is very important to examine the ignition and combustion properties of the Al-based nEMs as a potential heat transfer medium. In this work, we systematically investigated the effects of the addition of CB nanoparticles (NPs) on the ignition and combustion properties of Al/CuO NP-based nEMs (here Al NPs, CuO NPs, and CB NPs were used as the fuel metal, oxidizer, and heat transfer medium, respectively).

2. Experimental

2.1. Fabrication of CB/Al/CuO composites

In this study, Al, CuO, and CB NPs were mixed to fabricate CB/Al/CuO NP-based composite powders and pellets. Commercially available Al (NT base Inc., Korea), CuO (NT base Inc., Korea), and CB (Ketjenblack EC-300J, Akzo Nobel Functional Chemicals, USA) NPs with average particle sizes of 78 ± 2.3 nm, 130 ± 5.3 nm, and 47 ± 1.3 nm, respectively, were used without further modification. The fabricated CB/Al/CuO NP composites were ignited using a cylindrical burn tube to examine their ignition and combustion properties (Fig. 1).

To fabricate the Al/CuO-based nEM composites, Al NPs were mixed with CuO NPs in ethanol (EtOH) solution at an Al/CuO mixing ratio of 30:70 wt.%, which corresponded to the optimum combustion conditions [26–28]. After that, various amounts of CB NPs (0.0, 0.1, 0.3, 0.5, 1, 3, 5, and 10 wt.%) were added to the nEM-containing dispersion. To achieve a homogeneous dispersion of CB, Al, and CuO NPs in EtOH, it was sonicated for 30 min at a power of 200 W and frequency of 40 kHz. After drying the CB/Al/CuO NP-dispersed solution for 15 min inside a convection oven heated to 80 °C, the obtained CB/Al/CuO NP composite powders were characterized using a field emission scanning electron microscope (FE-SEM; Hitachi, Model S-4700) operated at a voltage of 15 kV and transmission electron microscope (TEM; FEI, Model Talos F200X) operated at a voltage of 200 kV. In addition, to examine ignition and combustion properties of CB/Al/CuO NP composite powders, a series of burn tube tests were conducted (see Fig. 1). Briefly, ~200 mg of the CB/Al/CuO NP composite powders were filled with in a polyethylene terephthalate (PETE) tube with a 3 mm in diameter and 50 mm in length, and then PETE tubes were inserted into a transparent acrylic block. The one end of burn tube was ignited using a hot-wire, and then the flame propagation toward the other end was recorded using a high-speed camera.

2.2. Characterization of ignition and combustion properties of CB/Al/CuO NP composites

To examine the ignition and combustion properties of the fabricated CB/Al/CuO NP composite powders and pellets, various characterization methods including pressure cell testing (PCT), temperature jump (T-jump) ignition testing, high-speed camera analysis, and thermogravimetric and differential scanning calorimetry (TG-DSC) were utilized. A PCT procedure was used to analyze the pressure traces and pressurization rates of the composite powders after their ignition inside a 13-ml sealed pressure cell [30]. It was conducted by placing 16 mg of the tested powder in the sealed pressure cell and igniting it with a hot tungsten wire at a current of 2 A and voltage of 1.5 V. The pressurization rate was calculated by measuring the maximum pressure and corresponding rise time after the tested powders were detonated. A high-speed camera (Photron, Model FASTCAM SA3 120 K, 30,000 FPS) was utilized to measure the burn rate and total burning time of the composite powder. To determine the ignition delay times of the fabricated CB/Al/CuO NP composites, they were subjected to a T-jump testing procedure [29–33]. Pt wire with a diameter of 10 μm was coated with the prepared CB/Al/CuO NP powder by mixing 20 mg of the tested composite with 200 mg of the EtOH:H2O solution with a mixing ratio of 4:45:56 wt.% [34] followed by the sonication for 30 min at a power of 200 W and frequency of 40 kHz. To measure the heat flow generated by various CB/Al/CuO NP composites, TG-DSC (Setaram, Model LABSYS evo) analysis was performed in a nitrogen gas environment and the temperature range from 30 °C to 1000 °C at a heating rate of 10 °C min⁻¹.

3. Results and discussion

According to the results of FE-SEM analysis, the fabricated CB/Al/CuO NP composite powders had spherical shapes and were highly aggregated (the average diameters of Al, CuO, and CB NPs...
were $78 \pm 2.3$ nm, $130 \pm 5.3$ nm, and $47 \pm 1.3$ nm, respectively; see Fig. 2).

The results of TEM analysis of the CB/Al/CuO NP composite with a CB content of 1 wt.% are shown in Fig. 3a. It should be noted that the Al NPs are surrounded by the passivation oxide layer with a thickness of approximately 3-4 nm (Fig. 3b). The elemental mapping and energy dispersive spectroscopy (EDS) analyses of the same powder (see Fig. 3c and d) revealed the presence of Al, Cu, O, and C elements, while the Al, CuO, and CB NPs were homogeneously mixed at the nanoscale (the observed Si species likely originated from the semiconductor detector of the TEM system.)

Figure 4a shows the pressure traces of the Al/CuO NP composites mixed with various amounts of CB NPs after their ignition inside the pressure cell. When 1−3 wt.% of CB NPs was added to the Al/CuO NP composite, the generated maximum pressure was close or slightly greater than that produced by the Al/CuO NP composite.
without CB NPs. However, the maximum pressure decreased when the content of added CB NPs exceeded 3 wt.%. Figure 4b shows the pressurization rates determined for various composite powders by calculating the ratio of the maximum pressure to the rise time (the steeper slopes of the pressure trace graphs indicate larger pressurization rates). The pressurization rates of the Al/CuO NP composites mixed with 1 – 3 wt.% of CB NPs were higher than that of the Al/CuO NP composite without CB NPs. However, their magnitudes significantly decreased after the addition of more than 3 wt.% of CB NPs to the composite matrix. The obtained results suggest that the presence of a critical amount of CB NPs (≤1–3 wt.%) in the Al/CuO NP composite strongly increases the maximum pressure and simultaneously decreases the rise time by rapidly transferring external heat energy to the Al/CuO NP composite matrix. However, the presence of excessive amount of CB NPs (>3 wt.%) can significantly deteriorate the combustion and explosive characteristics of Al/CuO composite matrix, because the external heat energy applied is rapidly dissipated, and simultaneously the oxidation of Al is thermochemically intervened by the excessive CB, which blocks the oxygen transfer from CuO.

To examine the propagation characteristics of the flame generated by the ignition of CB/Al NP/CuO NP composites, a series of burn tube tests were conducted. The effect of the addition of various amounts of CB NPs on the burn rate and total burning time of the Al/CuO NP composite powders was examined by performing the burn tube tests. Figure 5 shows the snapshots taken by the high-speed camera after the ignition of the CB/Al/CuO NP composite powders. The burn rate was calculated as the length of the burn tube (5 cm) divided by the total time required for the flame to propagate from its one end to the other end. The total burning time was also determined as the time passed between the beginning of the ignition and the reaching of flame at the end of burn tube. Once the CB-containing Al/CuO NP composite powder was ignited, its burn rate declined gradually with increasing amount of added CB NPs up to 3 wt.%. However, it significantly decreased at a CB NPs content greater than 3 wt.%. Simultaneously, the total burning time considerably increased with increasing amount of added CB NPs in a composite powder, suggesting that the addition of a critical amount of CB NPs to the Al/CuO NP composite matrix increased the magnitude of heat dissipation and, thereby, hindered the combustion of the fabricated Al/CuO NP composite powders.

To examine the effect of the amount of added CB NPs on the ignition delay time of the Al/CuO NP composite powders, a series of T-jump ignition tests were performed. The inset of Fig. 6 shows the sequential snapshots taken by the high-speed camera during the T-jump ignition of the Pt wire coated with the CB (1 wt.%)/Al/CuO NP composite powder. The ignition process began after a power of 2 W was supplied to the Pt wire for 155.267 ms, which corresponded to the actual ignition delay time (the ignition delay time in this study was defined as the time passed between applying the power and beginning of the ignition process). After activating the ignition process, the composite powder visually exploded. Figure 6 shows the ignition delay times of the Al/CuO NP composite powders containing various amounts of added CB NPs. Their magnitude monotonically decreased with increasing amount of added CB NPs, suggesting that the presence of CB NPs in the Al/CuO NP composite matrix
could reduce their ignition delay time due to the enhancement of the heat transfer properties.

DSC measurements in the nitrogen gas environment were performed to examine the effect of the CB NP addition on the total heat energy generated by the Al/CuO NP composites (Fig. 7). The obtained spectra show that exothermic reactions typically occur in the temperature range of 500—600°C, as indicated by the strong exothermic peaks centered at around 580°C. The calculated total heat energy generated by the Al/CuO NP composite without CB NPs was 1752 J g⁻¹. After increasing the amount of CB NPs in the Al/CuO NP matrix from 0.1 to 10 wt.%, the value of the total heat energy (∆Htotal) gradually decreased confirming that CB NPs could be used as a control medium for the self-propagating combustion and explosion reactions of the Al/CuO NP composites due to thermochemical intervention.
To demonstrate the effect of CB NPs as a control medium on the combustion and explosion reactions of the fabricated Al/CuO NP composite powders, a series of explosion tests were performed (see Fig. 8) [35]. During the sand dent experiments, 20 mg of the Al/CuO NP composites with various contents of added CB NPs were loaded and ignited on the surface of bentonite soil with around 50% theoretical density. After the combustion and explosion reactions were complete, craters with various diameters were created. When Al NP/CuO NP powders without CB NPs or with CB contents less than 1 wt.% were used, the diameters of the formed craters were around 20 mm. However, when the amount of CB NPs was greater than 1 wt.% the diameter of the crater significantly decreased. The obtained results confirm that the addition of a critical amount of CB NPs can improve the combustion and explosion characteristics of nEMs composites by affecting their heat transfer and thermochemical properties, and that CB NP additives can serve as an effective control medium for the ignition, combustion, and explosion reactions of nEMs in thermal engineering applications.

4. Conclusions

In this work, the effect of the CB NP addition on the ignition and combustion properties of the Al/CuO NP-based nEMs has been examined. The CB/Al/CuO NP composite powders were fabricated via simple sonication in EtOH solution followed by solvent evaporation. The presence of less than 1 wt.% of CB NPs in the Al/CuO NP-based nEMs increased their pressurization and burn rates due to the enhanced heat transfer in the self-propagating combustion reactions. However, the addition of excessive CB NPs (> 1 wt.%) to the Al/CuO NP-based nEMs significantly suppressed their combustion and explosion processes due to the external heat dissipation by rapid heat transfer and the thermochemical intervention in the self-propagating reactions by blockage of oxygen transfer from CuO NPs to Al NPs. The ignition delay time was monotonically reduced with the presence of CB NPs in the Al/CuO NP-based nEMs due to the enhanced heat transfer properties. The total heat energy was gradually decreased with increasing amount of CB NPs because of their thermochemical intervention in the exothermic reactions. Hence, CB NP-based additives can be used as a potential control medium, which strongly affects the heat transfer and thermochemical interactions between nEM components and allows precise tuning their ignition and combustion properties for various thermal engineering applications.
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