

**CORRELATION BETWEEN MICROSTRUCTURE AND EXOTHERMIC REACTION KINETICS OF Al-CuO THERMITE NANOCOMPOSITE POWDERS FABRICATED BY CRYOMILLING**

Al-CuO is a thermite material exhibiting the exothermic reaction only when aluminum melts. For wide spread of its application, the reaction temperature needs to be reduced in addition to the enhancement of total reaction energy. In the present study, a thermite nanocomposite with a large contact area between Al and CuO was fabricated in order to lower the exothermic reaction temperature and to improve the reactivity. A cryomilling process was performed to achieve the nanostructure, and the effect of composition on the microstructure and its reactivity was studied in detail. The microstructure was characterized using SEM and XRD, and the thermal property was analyzed using DSC. The results show that as the molar ratio between Al and CuO varies, the fraction of uniform nanocomposite structure was changed affecting the exothermic reaction characteristics.

*Keywords:* Al-CuO, Thermite, Nanocomposite, Cryomilling, High energy density materials

**1. Introduction**

When aluminum powder reacts with metal oxides at temperatures near its melting point, a large amount of energy is generated by the process of reducing the metal oxides because of the significant reducing power of aluminum. It can instantaneously generate extremely high temperatures in a small area, and the mechanism is similar to black gunpowder which is usually a mixture of fuel and oxidizer. This reaction is also called as thermite reaction originally developed in Germany [1-3]. When aluminum and metal oxide powders are simply blended without any special treatment, it is necessary to raise the temperature enough to initiate the exothermic reduction reaction either by external heat source or by high physical impact. Therefore, there is a strong need to lower the ignition temperature so that this thermite system can be widely utilized with reduced external input [4].

One of the methods to lower the reaction temperature is to form a composite structure with oxide-dispersed microstructure. In this case, the surface area of powder particles does not increase, so that the oxidation reaction can be suppressed in room temperature and air conditions for safety. Also, the composite structure has more contact areas between Al and metal oxide than the simple blend because the metal oxide particles are distributed in Al matrix particles, so that the exothermic reaction can be promoted at lower temperatures.

In the present study, cryomilling process was applied to achieve an Al-CuO nanocomposite powder. The cryomilling

involves attrition milling of powders in liquid nitrogen minimizing the reactions to prevent undesired explosion during the process. The cryomilling also accelerates grain refinement which can produce well-dispersed fine particle distribution in relatively shorter time [5-11]. Therefore, it is expected that using cryomilling technique, the finer composite structure can be achieved in shorter time suppressing unwanted reactions. In this research, microstructural evolution and corresponding variation of thermal property were investigated according to the molar ratio of Al to CuO.

**2. Experimental**

The initial powder was prepared by blending of spherical Al powders (99.99%, Changsung, Korea) with an average size of 5  $\mu\text{m}$  and CuO powders with an average size of 2  $\mu\text{m}$  (Kojundo Chemical Laboratory, Japan) in three different compositions of Al:CuO as 2:1, 3:1, and 4:1 in molar ratio. The powder blend was cryomilled in a 1L batch for 8 h at  $-160\pm 5^\circ\text{C}$  using liquid nitrogen. The ball-to-powder ratio was 30:1, and the impeller rotation speed was 180 rpm. Stearic acid of 0.15 wt.% was introduced into the cryomilling chamber as process control agent (PCA) to prevent excessive cold welding and agglomeration of powders.

Microstructure was investigated using a field emission scanning electron microscope (FE-SEM, LYRA3, Tescan) in backscattered electron (BSE) mode at 15kV, and phases were analyzed using an X-ray diffraction (XRD, Miniflex2, Rigaku)

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in 20~80° with 2°/min. Exothermic reaction behavior was determined using differential scanning calorimetry (DSC, DSC-404 F1/F3 Pegasus, Netzsch) up to 1200°C with a heating rate of 50°C/min.

### 3. Results and discussion

Figure 1 shows cross-sectional SEM images of cryomilled Al-CuO powders in three different compositions at a lower magnification. Most particles in all compositions appear to be a composite of Al-CuO by mechanical alloying as shown in brighter gray particles in Fig. 2. However, as the Al ratio increases, pure Al or Al-rich particles without CuO dispersion were more observed, shown in darker gray particles in Fig. 2. It is shown that CuO particles were barely found inside these Al-rich particles, but exist mostly on the surface. These Al-rich particles were cold-welded each other rather than alloyed with CuO particles, and they will deteriorate the total energy generated by the exothermic reactions.

In addition, in the 2:1 composition powders, relatively large CuO particles were occasionally observed as seen in white particle in Fig 1(a). Considering the size of this CuO particle, about 50  $\mu\text{m}$  in diameter, it is much larger than the original CuO particles before the cryomilling. Therefore, it is rather a cluster of CuO particles agglomerated during cryomilling. The 2:1 molar ratio of Al:CuO is the stoichiometrically ideal composition in which both Al and CuO materials can fully participate in the reaction without remnant so that the maximum exothermic energy can be achieved [12]. However, in 2:1 composition of the present study, some of CuO particles were not incorporated into the Al particles during cryomilling, but exist as agglomerated clusters of themselves. These particles also reduce the contact area between Al and CuO, and will lower the total amount of exothermic reaction.

Figure 2 contains higher magnification SEM images of cryomilled Al-CuO powders exhibiting the particle distribution of CuO in Al matrix powders. In all three compositions, brittle CuO particles were primarily uniformly dispersed in ductile Al particles. Most of dispersed CuO particles appear to be sub-micrometer size, while the initial particle size of CuO was 2  $\mu\text{m}$  in average.

It is noticeable that the 3:1 composition powder in Fig. 2(b) exhibited the shortest average distance between dispersed CuO particles which means the largest fraction of CuO among three compositions. The 2:1 composition sample showed the intermediate fraction of CuO particles, and the 4:1 composition sample showed the least fraction of CuO particles in the Al matrix. The molar ratios of 2:1, 3:1, and 4:1 between Al and CuO are equivalent to the volume ratios of 1.56:1, 2.34:1, and 3.12:1, respectively. In case of the 3:1 composition, the area fraction of CuO must be about 43% based on the stereology, but it is apparently more than 50% as seen in Fig. 2(b).

The reason that the 3:1 composition exhibit not the intermediate but the largest fraction of CuO is attributed to the existence

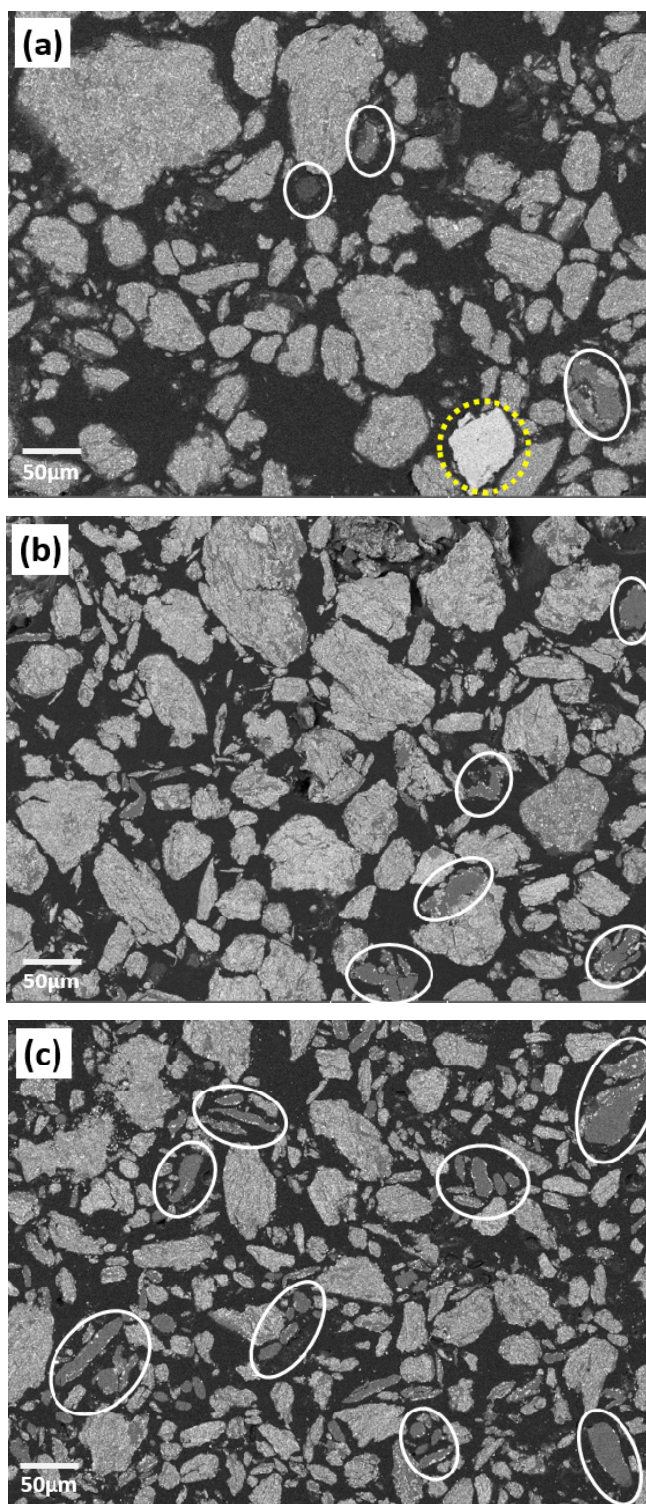


Fig. 1. Lower magnification cross-sectional SEM micrographs of cryomilled Al-CuO powders in different molar ratio of Al:CuO; (a) 2:1, (b) 3:1, (c) 4:1. White straight-lined circles indicate Al-rich particles, and yellow dot-lined circles indicate CuO clusters

of both CuO agglomerated clusters found in 2:1 composition and Al-rich particles observed in 4:1 composition, as previously shown in Fig. 1. The 2:1 composition sample is supposed to exhibit the largest fraction of CuO, but it was not because CuO particles were agglomerated forming clusters. Also, the 4:1 composition sample must have the least fraction of CuO, but it

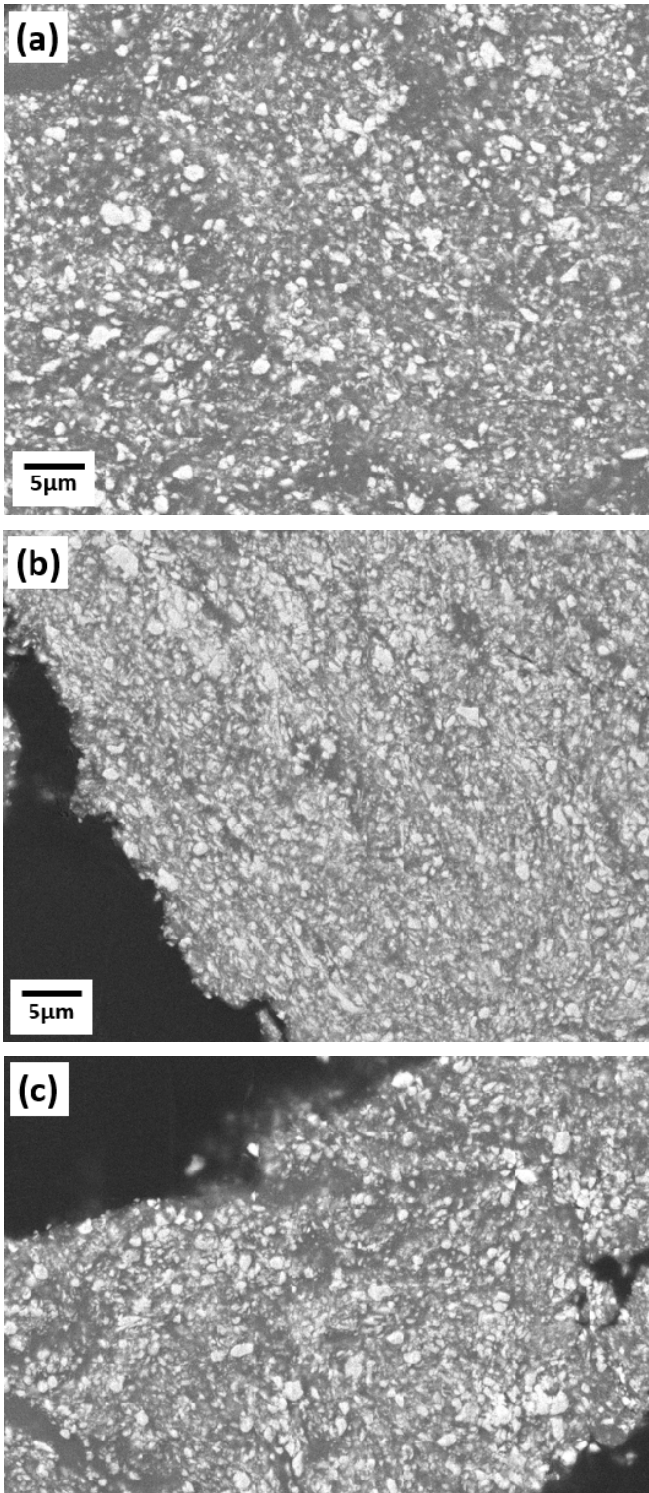


Fig. 2. Higher magnification cross-sectional SEM micrographs showing size and distribution of CuO inclusions in the mechanically allowed composite powders in different molar ratio of Al:CuO; (a) 2:1, (b) 3:1, (c) 4:1

was similar to the 2:1 composition sample due to the existence of incompletely milled Al particles.

Figure 3 shows XRD patterns of Al-CuO composite powders in three different compositions. Pure Al and CuO peaks were primarily observed in all compositions. However, slight intensity of Cu<sub>2</sub>O peaks were additionally found in 4:1 composition, while

the 2:1 and 3:1 compositions showed only pure Al and CuO peaks. During the milling, Al powders were repeatedly fractured and cold-welded. By these processes, thin oxide layers on the Al surfaces were broken, and the reactivity increases because of the fresh Al surfaces without oxide layers. The excessive amount of reactive Al contents in the 4:1 composition increases probability to react with CuO particles so that the CuO is partially reduced forming Cu<sub>2</sub>O phase. Therefore, it can be said that the Cu<sub>2</sub>O observed in the 4:1 composition is a product of partial reduction of CuO by excessive Al contents shown in Fig. 1(c) during cryomilling. Because the Al-CuO thermite material in this study generates a large amount of energy by simultaneous massive reduction of CuO with Al, the existence of partially reduced Cu<sub>2</sub>O in 4:1 composition will also adversely affect to the total energy generation.

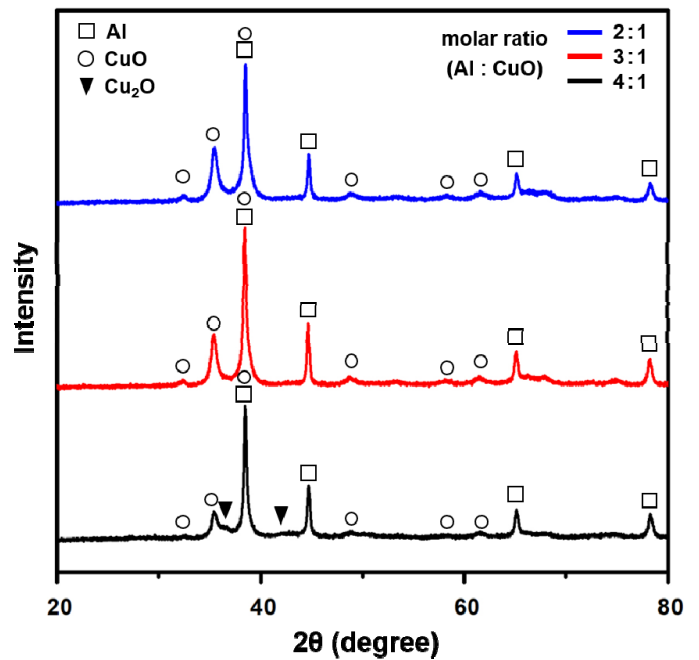


Fig. 3. X-ray diffraction patterns of cryomilled Al-CuO composite powders with various compositions

Figure 4 exhibits the results of DSC analysis for Al-CuO composite powders in three different compositions. The reaction initiation temperature and the amount of heat generation in this thermite material can be interpreted from these DSC curves. First, the reaction initiation temperature, also regarded as ignition temperature, is determined from the inflection point at the steep increase in heat flow curve immediately prior to the major exothermic peak at 600°C. The ignition temperatures for the Al-CuO thermite powders were 540, 598, and 587°C for the 2:1, 3:1, and 4:1 compositions, respectively. The 2:1 composition exhibited the lowest ignition temperature, however not the 4:1 but the 3:1 composition showed the highest ignition temperature. Secondly, the amount of heat generation, also regards as ignition calories, is determined from the area integral under the heat flow curve. It is apparent from Fig. 4 that the total heat calories were the lowest in the 2:1, intermediate in the 4:1, and

the largest in the 3:1. This variation is the same as the trend of reaction initiation temperature above. Therefore, both ignition temperature and ignition calories are independent of the Al composition, but is rather related to the amount of composite structure. As seen in Fig. 1 and 2, the 3:1 composition showed the largest amount of composite powders with well-dispersed CuO particles while the 2:1 and 4:1 showed CuO clusters and Al-rich particles, respectively. The 3:1 composition material also has the largest fraction of CuO dispersion within the Al particle which enhances the total reactivity due to the shorter reaction distance and to the larger contact area between Al and CuO.

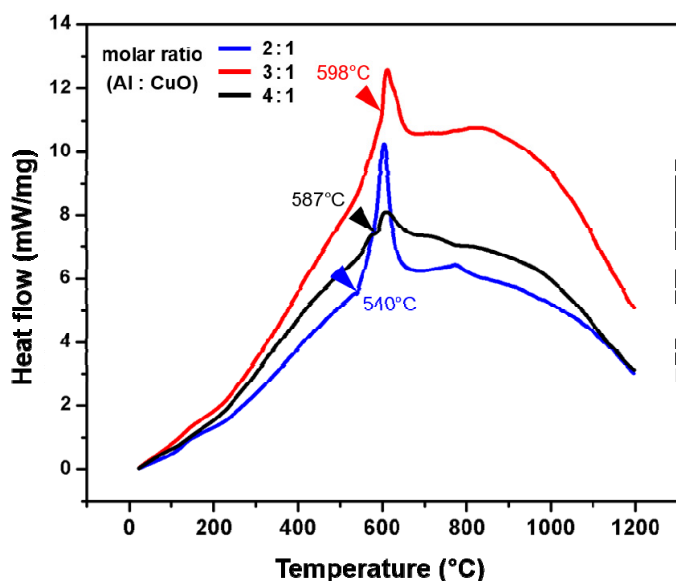


Fig. 4. DSC heat flow curves of cryomilled Al-CuO composite powders with various compositions. The arrows indicate the reaction initiation temperatures

In comparison of three composition materials in terms of ignition characteristics, it can be said that the 2:1 composition has greater stand-alone usability because of its lower reaction initiation temperature. It is attributed to the fact that the 2:1 is the ideal stoichiometric molar ratio between Al and CuO and is expected to have most outstanding ignition characteristics among three compositions. However, in case external energy is provided assisting the initiation of the exothermic reaction, such as external heat or impact energy, the 3:1 composition is most efficient because it generates the largest amount of the total ignition calories. It is concluded that the uniform nanocomposite structure achieved by cryomilling was a decisive factor for the overall exothermic reaction kinetics of Al-CuO thermite material.

#### 4. Conclusions

The Al-CuO thermite nanocomposite powders were successfully fabricated using cryomilling technique with three different molar ratio of Al to CuO, 2:1, 3:1, and 4:1. In general, the

harder CuO inclusions were well distributed within the softer Al particles in all three compositions. However, agglomerated CuO clusters were found in the 2:1 composition, while excessive Al powders remained as incompletely milled powders in the 4:1 composition. The XRD analysis showed that partially reduced CuO was found as Cu<sub>2</sub>O in the 4:1 composition. Therefore, the 3:1 composition sample showed less amount of features which adversely affect to the exothermic reactions, compared with other compositions. In the thermal analysis, the 2:1 composition exhibited the lowest ignition temperature, but the 3:1 composition showed much larger amount of the total ignition energy compared with other compositions because there were more fraction of fine CuO inclusions in the composite powders in the 3:1 composition. Although the 2:1 composition is the stoichiometrically ideal molar ratio between Al and CuO, the results indicated that the 3:1 composition with external assist of ignition is most efficient as a high energy density thermite Al-CuO. Also, the feasibility of making the nanocomposite Al-CuO thermite was achieved by using cryomilling technique.

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