Tailoring oxidation of Al particles morphologically controlled by carbon nanotubes

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A B S T R A C T
Aluminum powder is used for energetic materials due to high energy density. Controlling oxidation rate, oxidation temperature, and reaction enthalpy is important parameters prior to practical use. Here, we engineered static and dynamic properties of oxidation of Al particles by mixing CNTs (carbon nanotubes) having high thermal conductivity and large exothermic energy. Morphologies of Al/CNT mixture were engineered by a mechanical pulverization. Among various morphologies of Al/CNT mixture of i) CNTs adhered on the surface of Al particles, ii) CNTs partially embedded onto Al particles, forming an urchin type, and iii) CNTs fully embedded into aggregated Al particles, urchin type Al/CNT revealed the largest exothermic enthalpy at the lower oxidation temperature for both \( \gamma \)-Al\(_2\)O\(_3\) and \( \alpha \)-Al\(_2\)O\(_3\) phases. This was attributed to the fast heat transfer into Al particles via partially embedded CNTs. Large exothermic enthalpy as well as the mass of alumina were obtained in oxidation of Al/CNT mixture compared to pure Al particles up to 1000°C oxidation. The exothermic enthalpy showed strong dependence on the CNT content, increasing to \( \approx 188 \) kJ/g at 20 wt% CNT. The engineering ability of thermal properties in Al particles with CNTs opens a new research area for diverse use of solid fuel Al.

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1. Introduction

Al (Aluminum) is widely used as an energetic material of propellants, pyrotechnics, and explosives because of its high energy density generated during oxidation [1,2]. One key parameter for ignition mechanism of Al particles is the heating rate. At slow heating rate (<10 K/s), DOM (diffusion oxidation mechanism) is dominant [3–6]. Oxidation of Al particles occurs in four stages from 300 to 1500°C, classified by phase transformation of alumina shell: i) growth of shallow \( \alpha \)-Al\(_2\)O\(_3\) (amorphous alumina) layer by natural oxidation under ambient conditions, ii) formation of \( \gamma \)-Al\(_2\)O\(_3\) occurred in the temperature range of 550°C, involving rupturing of \( \gamma \)-Al\(_2\)O\(_3\) due to phase transformation and volume expansion of Al particles, iii) healing surface of Al particles into the formed cracks which occurs with phase transition of Al\(_2\)O\(_3\), and iv) formation of \( \alpha \)-Al\(_2\)O\(_3\) enlarged by further oxidation which occurs in the temperature range of 970°C. On the other hand, at fast heating rate (10\(^6\)–10\(^8\) K/s), MDM (melt dispersion mechanism) is dominant [7–11]. In this case, temperature reaches quickly melting temperature of Al before cracking of alumina occurs so that Al inside particles starts melting, rupturing a-Al\(_2\)O\(_3\) shell instead of local cracks observed in DOM due to the build-up of high dynamic pressure within Al particles. An unloading pressure wave then propagates to the center of the particles and disperses the molten Al particles into small clusters at high velocity, leading to ignition of small Al clusters [10,11].

Recently, there have been several reports on strengthening Al mechanical strength adding CNTs (carbon nanotubes) [12–14] due to their high mechanical strength (tensile strength: 150 GPa) [15]. Nevertheless, the related thermal properties of Al/CNT composite have been rarely investigated in spite of high thermal conductivity and high exothermic energy during oxidation of CNTs. It has been reported that an exothermic reaction was observed by forming Al
carbides under N₂ ambient [16]. On the other hand, control of oxidation temperature, exothermic energy, phase transition from γ-Al₂O₃ to α-Al₂O₃ phase, formation of aluminum carbide, and oxidation rate of Al particles are of critical importance for the use of Al particles to propellants and pyrotechnics. Several attempts have been reported: addition of metal oxides [17–19], coating of Al particles by other metals and fluorine [20], and miniaturization of Al particles [21–23]. Yet, the underlying mechanism for the change of thermal properties of these materials has not been clarified in general. It has been reported that CNTs can be ignited by photographic flash, which is assisted by the presence of iron particles [24–27]. This suggests that the thermal properties of Al particles could be significantly modified so as to be beneficial for future applications of Al particles.

The purpose of this paper is i) to control thermal properties of Al particles by introducing various contents of CNTs, ii) to clarify the underlying mechanism for the role of CNTs depending on the clustering conditions of Al particles with CNTs, and iii) to control sizes of Al particles by adding different content of CNTs. In this report, we fabricated various types of Al/CNT mixture by a simple mechanical pulverization under Ar ambient. Three phases in the morphology of Al/CNT mixture were distinct; i) Stage I, CNT-coated Al particles, ii) Stage II, CNTs embedded partially inside fractured Al particles, while some portion of CNTs remained on the surface of Al particles, and iii) Stage III, reaggregation of Al particles with fully embedded CNTs. We measured oxide mass, phase transition temperature for oxide, exothermal energy depending on stages and CNT content by using Raman spectroscopy, TGA (thermogravimetric analysis), XRD (X-ray diffraction), and DTA (differential thermal analysis). The capabilities of controlling thermal properties using CNTs are discussed in detail in terms of CNT content and Al/CNT morphology.

2. Material and methods

2.1. Fabrication of Al/CNT mixture

MWCNTs (Multiwalled carbon nanotubes) (CM95, Hanwha, Korea) were mixed with Al powder (Samjeon Chemicals, 200 mesh, Korea) via planetary type ball miller (J.E.Powder, Korea). The MWCNTs which have 10–30 nm of diameter and few μm in length were used as a lubricant. The zirconia balls which are 5 mm in diameter were used as an impact medium. In order to prevent Al oxidation, the mixing process was performed in a glove box (M.O.Tech, Korea). The glove box was filled with Ar gas. The content of MWCNTs was 5 wt%, 10 wt%, and 20 wt% respectively. For comparison purpose, the total weight of Al and MWCNTs is fixed at 150 g. The BPR (ball to powder ratio) was fixed to 1/4. The ball milling times were 0.5, 1, 2, and 3 h at 250 rpm.

2.2. Structural characteristics of Al/CNT mixture

The morphologies of Al/CNT mixture were characterized by FE-SEM (field-emission scanning electron microscopy) (JEOL 7000F, Jeol, Japan). Raman spectroscopy (RM 1000, 2.41 eV, Renishaw, Invia) was used to measure the crystalline evolution of MWCNTs according to milling time. For Raman sample preparation, Al was etched by HCl (hydrochloric acid) to obtain remaining CNTs. After etching Al, acid was rinsed with DI (deionized) water several times. The obtained CNT powder was placed in dry oven for 24 h at 70 °C. BET (Brunauer Emmett Teller) (ASAP 2020 instrument, Micromeritics, USA) surface area analysis was measured by nitrogen adsorption/desorption isotherms at 77 K using a static volumetric technique. The crystalline structure and phase transition of Al/CNT mixture were confirmed by powder-XRD (D8 FOCUS, Bruker AXS, Germany) using Cu Kα radiation (1.54 A) at 1.6 kW.

2.3. Thermal characteristics of Al/CNT mixture

The weight changes of the burned CNTs and Al oxide were measured with TGA (Q500, TA instruments, USA). The sample weight was 40 ± 6 mg. The samples were pretreated up to 200 °C with a ramping rate 20 °C/min to remove moisture and kept for 30 min under N₂ gas ambient and then cooled down to room temperature. And then, the samples were heated up to 1000 °C with a heating rate 5 °C/min under air gas ambient. The thermal reaction of Al/CNT composite was measured with DTA (TG/DTA7300, SEKO, Japan). The initial powder weight was chosen to be heavier than 12 mg. The reaction process was investigated at a heating rate of 5, 10, 20 °C/min up to 1300 °C.

3. Result and discussion

Fig. 1 shows morphological changes of Al/CNT mixtures as a function of mechanical ball milling time. The morphology of Al/CNT mixture can be classified into three types with evolution of milling time: Stage I, CNTs are coated on the surface of Al particles and spherical Al particles are distorted into rather platelet forms, Stage II; Al particles are disintegrated into small sizes and CNTs are partially embedded inside fractured Al particles, while portion of CNTs remains on the Al surface, forming an urchin shape, and Stage III; Al/CNT particles are further reaggregated into large-sizes. In early Stage I, CNTs were dispersed by the ball milling and further coated on Al particles, while the size of Al particles was not altered appreciably. In intermediate Stage II, the size of Al particles was decreased from 10–70 μm to 2–4 μm by further mechanical ball milling process. In final Stage III, the size of Al particles was increased to more than 100 μm by reaggregation. CNTs were completely embedded into reaggregated Al particles. It is worth noting that ball milling without CNTs leads to a simple sticking of Al particles. Thus, CNTs act as a lubricant by being adsorbed on the surface of Al particles to prevent aggregation of Al particles at initial stage. This leads to the formation of several morphology stages. Our main concern is the peculiar thermal properties of Al/CNT mixtures which will be described later.

Fig. 2a shows Raman spectra of Al/CNT (10 wt%) mixture in terms of stages with different ball milling times. CNTs of 10 wt% were fixed for analysis unless specified. The pristine CNTs show D-band near 1340 cm⁻¹, sp² characteristic of defects on CNTs, and G-band near 1580 cm⁻¹, sp² characteristic of hexagonal carbons [28]. The intensity ratio of D-band to G-band increased as the ball milling time raised, as shown in Fig. 2b. The intensity ratio increased linearly at Stage I and was saturated at Stage II. Further change was not observed at Stage III. Although CNTs were damaged during ball milling to some degree as indicated by the increased intensity ratio, the tubular shape of CNTs was still retained, as shown in Fig. 1. Fig. 2c shows Brunauer Emmett Teller (BET) surface area for Al/CNT mixture. With increasing ball milling time, the CNTs were dispersed and attached on the surface of Al particles (see inset). Thus the BET surface area of CNTs kept increasing during Stage I. With further increasing of ball milling time, CNTs started embedding into Al particles, hence reducing BET surface area during Stages II and III. Small BET surface area was still obtained even at 150 min, indicating the presence of CNTs on the surface of Al particles. No BET area was observed at 180 min, where all the CNTs were embedded and Al particles were reaggregated, in good correlation with SEM images in Fig. 1. The damage of CNTs was also confirmed by the diminished peak near 26° in XRD spectra. Al(111) peak was broadened compared to the pristine Al as the ball milling time...
Fig. 1. Morphological modifications of Al/CNT mixtures with ball-mill time: (a) Stage I (30 min); CNTs coated on the surface of Al particles, (b) Stage II (120 min); CNTs embedded inside Al particles while portion of CNTs remain on the Al surface, and (c) Stage III (180 min); Aggregation of Al particles with embedded CNTs inside.

Fig. 2. Characteristics of Al/CNT (10 wt%) mixtures: (a) Raman spectra, (b) intensity ratio of D-band to G-band of Raman spectra for ball-milled CNTs at different times without Al, (c) BET surface area as a function of ball milling time, and (d) XRD including pure Al.
increased, implying embedment of CNTs inside Al particles (See Supplementary Information Fig. S1).

In order to investigate the effect of CNTs on oxidation of Al particles, TGA was performed under air ambient, as shown in Fig. 3a. Oxidation of pure Al particles occurred near 580 and 970 °C where oxidation temperature can be defined by the peak of differential weight of TGA curve, as shown in Fig. 3b. The first oxidation peak of pure Al near 580 °C is known as a γ-Al2O3 phase and the second peak near 970 °C as a α-Al2O3 phase, in agreement of typical route of phase transformations in alumina layer; α-Al2O3 → γ → δ → θ → α-Al2O3 [29]. An α-Al2O3 transforms to thermodynamically more stable crystalline polymorphs as the layer thickness reaches a critical value [30]. An α-Al2O3 transforms to γ-Al2O3 phase accompanied by cracking of alumina surface and healing in the temperature range of 530–590 °C (Fig. 3b), that is below Al melting temperature. Once the oxidation to form γ-Al2O3 phase is done, the oxide layer thickness reaches a critical thickness to form α-Al2O3 phase, which occurs near 970 °C [30]. SEM (scanning electron microscopy) image taken after 700 and 1000 °C oxidation shown in the insets of the first panel in Fig. 3b demonstrates a morphological difference between melted Al (700 °C) and particulate alumina (1000 °C).

On the other hand, oxidation behavior of Al/CNT (10 wt%) mixture is markedly different from pure Al sample. The weight of Al/CNT mixture was reduced during the initial stage of oxidation (400–600 °C), as shown in the second panel from top of Fig. 3a. This was ascribed to the burning of CNTs located on the surface of Al particles. As the ball milling time increased, the initial burning temperature was further lowered due to the damage to CNT walls and furthermore the burning amount was reduced due to the embedment of CNTs inside Al particles (See Supplementary Information Fig. S2). The weight increase near 600 °C due to the formation of γ-Al2O3 phase by oxidation Al particles was almost nullified by the reduction of weight by the CNT burning. The formation temperature of α-Al2O3 phase was shifted down to 907 from 970 °C of pure Al. The weight increase reached 145%, which is much larger than that of pure Al, was attributed to the enhanced oxidation by the presence of CNTs on the surface Al particles. This phenomenon was well corroborated with particulate morphology of SEM image in the inset of Fig. 3b even at 700 °C.

![Fig. 3. (a) TGA profile under air ambient at a ramping rate of 5 °C/min for different stage; Stage I (60 min), Stage II (120 min), and Stage III (180 min). The inset image shows schematic of Al/CNT mixture morphology and (b) the corresponding DTG (derivative thermogravimetry). The inset shows SEM image of Al/CNT mixture taken after TGA terminated at 700 and 1000 °C. Note that the scales in y-axes in (b) are different from each other, which is done to visualize each peak.](image1)

![Fig. 4. Oxidation characterization with CNTs of 10 wt% for different stages; (a) oxide weight and (b) oxidation temperature.](image2)
At Stage II, where CNTs are mostly embedded inside Al particles, while some portion of CNTs remained on the surface Al particles, the weight decrease by the burning of CNTs located on the surface of Al particles was negligible and the mass increase by Al oxidation became dominant to form distinct oxidation peak near 570 °C of γ-Al₂O₃ phase. In this case, one additional broad peak was observed near 827 °C. This was due to early oxidation of Al particles by the embedded CNTs that enhanced thermal conductivity within the particles. The heat transfer was more efficiently facilitated within Al particles so that Al was oxidized at lower temperature. This peculiar oxidation was attributed to extremely high thermal conductivity of CNTs (5000 W/mK) compared that of Al (237 W/mK). Nevertheless, the embedment of CNTs is inhomogeneous within Al particles, still revealing large peak of α-Al₂O₃ phase near the similar temperature range (936 °C) of pure Al. Both particulate alumina and aggregated alumina were consistently observed from SEM images.

At Stage III, where all the CNTs were embedded inside Al particles and particles were aggregated, no weight decrease was observed as expected. Oxidation temperature to form γ-Al₂O₃ phase increased to 652 °C. The decrease of oxidation temperature of α-Al₂O₃ phase was attributed to efficient heat transfer by the embedded CNTs. Correspondingly, the aggregated alumina was not observed in the SEM images but instead a whisker type of embedded CNTs. Correspondingly, the aggregated alumina was not observed in the SEM images but instead a whisker type of embedded CNTs. The formation of alumina phases was confirmed by XRD (Fig. 5). Al/CNT (10 wt%) mixture was heated in air to a selected temperature (700 and 1000 °C) at a scan rate of 5 °C/min, followed by natural cooling. With heat treatment in air at 700 °C, γ-Al₂O₃ phase noticeably appeared in Stage I of Al/CNT (10 wt%) mixture. This peak became strong at Stage II with additional appearance of aluminum carbide (indicated by red (in the web version) triangles). At Stage III, peaks of γ-Al₂O₃ phase (indicated by purple (in the web version) dots) were diminished and aluminum carbide peaks were in turn developed. Since the reaction temperature was limited at 700 °C, no α-Al₂O₃ phase was formed. On the other hand, with heat treatment at 1000 °C, formation of α-Al₂O₃ phase (green dots in the web version) was dominant in all stages. In particular, Al peaks disappeared almost completely at Stage II, as shown in Fig. 5b. Since Al particle sizes were small with partially embedded CNTs, oxidation of pure Al was increased by 12.8%, where most of initially formed γ-Al₂O₃ phase at around 580 °C was converted to α-Al₂O₃ phase at 970 °C. The weight of oxide for Al/CNT (10 wt%) mixture was increased to 58% till Stage II at 1000 °C, clearly indicating the CNT-assisted oxidation of Al particles via highly efficient heat transport by partially embedded CNTs inside Al particles. At Stage I, the weight of oxide was still larger than that of pure Al. The presence of CNTs on the surface of Al particles enhanced oxidation of Al by exothermic heat during burning. It is intriguing to see that the weight of oxidation was significantly decreased at Stage III. This difference originates from CNT morphology, as described in Fig. 1. While partially embedded CNTs (urchin shape) transport heat efficiently by picking up heat from the remaining protruded CNTs on the surface in Stage II, fully embedded CNTs in Stage III cannot accommodate heat transfer from outside Al particles in addition to large size of aggregated Al particles. This reduces efficiency of oxidation of Al particles. Formation of aluminum carbide inside Al particles could be another reason to prevent further oxidation due to poor thermal conductivity of aluminum carbide, although the weight of aluminum carbide was negligible. The values of the oxide weight shows: Stage II > Stage I > Stage III > pure Al. The formation temperature of γ-Al₂O₃ phase did not show a systematic change, as shown in Fig. 4b. On the other hand, the formation temperature of α-Al₂O₃ phase decreased up to Stage II by the enhanced heat transfer from partially embedded CNTs and slightly increased at Stage III by the similar reasons described above. Table 1 summarizes oxidation temperature range and the related oxidation rate. Inclusion of CNTs increased clearly the oxidation rate compared to pure Al. The fastest oxidation rate was observed for γ-Al₂O₃ phase in Stage II. Although Stage I gives the fastest oxidation rate at α-Al₂O₃ phase, oxidation rate of α-Al₂O₃ phase was complicated due to the split peaks in Stage II by the early formation of alumina near 827 °C.

The formation of alumina phases was confirmed by XRD (Fig. 5), Al/CNT (10 wt%) mixture was heated in air to a selected temperature (700 and 1000 °C) at a scan rate of 5 °C/min, followed by natural cooling. With heat treatment in air at 700 °C, γ-Al₂O₃ phase noticeably appeared in Stage I of Al/CNT (10 wt%) mixture. This peak became strong at Stage II with additional appearance of aluminum carbide (indicated by red (in the web version) triangles). At Stage III, peaks of γ-Al₂O₃ phase (indicated by purple (in the web version) dots) were diminished and aluminum carbide peaks were in turn developed. Since the reaction temperature was limited at 700 °C, no α-Al₂O₃ phase was formed. On the other hand, with heat treatment at 1000 °C, formation of α-Al₂O₃ phase (green dots in the web version) was dominant in all stages. In particular, Al peaks disappeared almost completely at Stage II, as shown in Fig. 5b. Since Al particle sizes were small with partially embedded CNTs,

<table>
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<tr>
<th>Sample</th>
<th>First oxidation (γ-Al₂O₃ phase)</th>
<th>Second oxidation (α-Al₂O₃ phase)</th>
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<tbody>
<tr>
<td></td>
<td>Temperature range (°C)</td>
<td>Oxidation rate (%/min)</td>
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<tr>
<td>Pure Al</td>
<td>536–649</td>
<td>0.11</td>
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<tr>
<td>Stage I</td>
<td>580–660</td>
<td>0.89</td>
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<tr>
<td>Stage II</td>
<td>455–669</td>
<td>1.84</td>
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<tr>
<td>Stage III</td>
<td>615–715</td>
<td>0.37</td>
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Table 1 Oxidation rate for different stages of Al/CNT (10 wt%) mixture.
oxidation was efficient to oxidize whole Al particles. Aluminum carbide (red triangles in the web version) as well as $\alpha$-Al$_2$O$_3$ phase was formed at Stage III. These observations are in congruent with TGA analysis discussed in the previous paragraph.

Fig. 6 shows the DTA curves of Al/CNT mixture and exothermic and endothermic enthalpy. Enthalpy was calculated by the area of DTA curves,

$$\Delta H_{\text{lit}} = \frac{\Delta H_{\text{cal}}}{c} \times a$$  \hspace{1cm} (2)$$

where $\Delta H_{\text{lit}}$ represents the real value of enthalpy of reaction (mJ/mg), $\Delta H_{\text{cal}}$ is the calculated value of area of DTA curves ($\mu$V s/mg), and $c$ and $a$ are constants of machine, (5202.06 $\mu$W and 0.5 $\mu$V, respectively). Endothermic reaction occurred due to the melting of Al particle at 666 °C, as shown in the top panel of Fig. 6a. The first peak of exothermic reaction of pure Al was not obvious and occurred at 601 °C due to oxidative conversion of Al into $\gamma$-Al$_2$O$_3$ phase before Al melting. The second broad peak near 1020 °C was observed due to transition to $\alpha$-Al$_2$O$_3$ phase. On the other hand, Al/CNT mixture showed apparent two exothermic reactions and one endothermic reaction. The first exothermic broad peak near 583 °C originates from Al oxidation before Al melting and burning of CNTs located on the surface of Al particles. The exothermic reaction temperature (583 °C) was decreased at Stage I compared to that of pure Al. The second exothermic peak near 967 °C became prominent due to the enhanced oxidation by the presence of CNTs inside Al particles. At Stage II, the exothermic temperature was further decreased to 558 °C and moreover exothermic enthalpy was increased due to the enhanced heat transfer rate into small-sized Al particles by the partially embedded CNTs. Stage II shows two additional exothermic peaks near 842 and 997 °C due to conversion from $\gamma$-Al$_2$O$_3$ phase to $\alpha$-Al$_2$O$_3$ phase in addition to further burning of CNTs embedded inside Al particles, leaving the largest exothermic enthalpy, as shown in Fig. 6a. At Stage III, the first exothermic reaction peak became blurred due to aggregated Al particles into large sizes and a complete embedding of CNTs into Al particles, in good agreement with surface morphologies in Fig. 1. At higher temperature, the second exothermic peak near 950 °C became broad due to the subsequent burning of CNTs embedded in Al particles. Total exothermic enthalpy of pure Al was $-10.2$ kJ/g due to partial oxidation, which is smaller than $-62.1$ kJ/g of completely oxidized Al [1]. This value became large with CNT inclusion, as summarized in Fig. 6b. The total exothermic enthalpy was $-121$ kJ/g, maximum at Stage II, which is ascribed to the enhanced oxidation of small-sized Al particles and burning of CNTs (Fig. 6b). The exothermic enthalpy by the burned CNTs (10 wt%) was estimated to be $-99.8$ kJ/g (See Supplementary Information Fig. S3). The exothermic enthalpy of Al oxidation contributed by CNT burning was estimated to be $-120.2$ kJ/g.

It is interesting to see endothermic enthalpy changes associated with Al melting (Fig. 6c). Enthalpy value of Al/CNT mixture was consistently reduced independent of the stages. This clearly demonstrates that the thermal properties of Al can be significantly modified by the inclusion stages. The corresponding activation barriers can be also extracted by fitting Kissinger and Crane equations (See Supplementary Information Fig. S4) [15,31,32]. The results are summarized in Table 2. Independent of the CNT inclusion, both $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ phases revealed nearly the first order kinetics with $n \sim 1$. This implies that the thermodynamics of Al/CNT mixture is governed by the first order kinetics. In the case of $\gamma$-Al$_2$O$_3$ phase, the activation barrier was lowered by the inclusion of CNTs (Table 2). In other words, the formation of $\gamma$-Al$_2$O$_3$ phase was accelerated by the inclusion of

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<th>Table 2</th>
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<td>Values of activation energy of pure Al and Al/CNT (10 wt%) mixture (Stage II) at reaction order, $n = 1$. $\gamma$-Al$_2$O$_3$ peak was split into two peaks near 827 and 936 °C.</td>
</tr>
<tr>
<td>Oxide phase</td>
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<tr>
<td>$\gamma$-Phase</td>
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CNTs. On the other hand, $\alpha$-$\text{Al}_2\text{O}_3$ phase was split into two peaks near 827 and 936 °C, as shown in Fig. 3b. The activation barrier height of the first peak near 827 °C was again lowered similar to that of $\gamma$-$\text{Al}_2\text{O}_3$ phase. In contrast, however, the activation barrier of the second peak was increased to 513 kJ/mol compared to 413.5 kJ/mol of pure Al. The origin of this change is not clear at the moment but could be attributed to the strengthened or compressively strained Al bonds, which exist due to inhomogeneous distribution of CNTs. Still the overall oxide mass during reaction was increased significantly due to the formation of nanosized Al particles.

We now discuss about the effect of CNT compositions, as shown in Fig. 7. At Stage I, the weight of oxide was increased as the CNT content increased in spite of mass reduction by the CNT burning. This can be explained again by the efficient oxidation of Al particles due to the burning of CNTs present at the surface of Al particles. At Stage II, where CNTs are partially embedded inside Al particles, oxidation became the most efficient among other stages, revealing...
increase of oxide mass except sample with 20 CNT wt%, which is equivalent to 45 vol%. This implies that most of CNTs were not in close contact with Al particles and thus the heat transfer by the burning of such CNTs becomes less efficient to oxidize Al particles. At Stage III, where all the CNTs were embedded and Al particles are reaggregated, oxide mass decreased accordingly. At 20 wt% CNT, no reaggregation was observed due to excessive CNTs on the surface of Al particles. Exothermic enthalpy was increased as the CNT content increased, and did not follow the trend of oxide mass changes. This means that the exothermic reaction is dominated mostly by the burning of CNTs. Endothermic enthalpy by the melting of Al followed the similar trend of exothermic enthalpy. The trend of diameter change with CNT content was also shown in Fig. 7c. Although the particle sizes became large at Stage III up to 10 wt%, no aggregation of particles was observed at 20 wt%.

We now discuss CAOM (carbon nanotubes-assisted oxidation mechanism) in Fig. 8. The mechanism of conventional Al oxidation is divided to two models: DOM [3–6] and MDM [7–11] by heating rate, as explained in the Introduction (Fig. 8a and b). On the other hand, the oxidation mechanism of Al/CNT mixture is categorized by three different phases in our work (Fig. 8c). At Stage I, CNTs that are present on the surface of Al particles are burned first, followed by formation of alumina. This process is similar to DOM at a slow heating rate except the increase of oxide mass. At Stage II, CNTs are partially embedded into Al particles, bridging heat transfer, accelerating Al liquidation inside particles. Liquid Al is expelled outside to eventually form γ-Al2O3 phase. Thus oxidation region of Al particles is expanded. In addition, some CNTs located inside Al particles start burning, which again accelerated Al liquidation and eventually most of Al particles are transformed into α-Al2O3 phase. At Stage III, oxidation process is rather slow at the beginning since almost all the CNTs are embedded and also Al particles become bigger due to reaggregation. With increasing temperature, CNTs embedded inside Al particles start burning, eventually increasing oxide mass.

4. Conclusion

We have shown carbon nanotubes-assisted oxidation of Al particles. Al/CNT mixture is classified with three types (Stage I, Stage II, and Stage III) which are formed by varying ball milling time: i) CNTs are distributed over the surface of Al particles, ii) CNTs are partially embedded into small-sized Al particles, forming an urchin shape, and iii) CNTs are fully embedded into reaggregated Al particles. CNTs play a role of lubricant during ball milling to prevent reaggregation of Al particles and as a consequence, Al nanoparticles with CNTs were produced. We found that thermal properties of Al could be modified significantly by adding CNTs. Exothermic reaction of CNTs by burning accelerated oxidation of Al particles: Oxidation temperature was reduced. Exothermic enthalpy was increased. Oxide mass was increased. Oxidation rate was increased, while oxidation rate is strongly dependent on the CNT content and morphology of Al/CNT mixture. Activation energy to transform from amorphous alumina to γ-alumina phase and from γ-alumina phase to α-alumina phase was reduced. The modification of oxidation of Al particles in the presence of CNTs can be utilized in energetic materials.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.energy.2013.04.039.

References


