Electrically conductive property of dense alumina/nano-carbon network composite fabricated by combination of gelcasting and argon sintering

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Alumina and nano carbon network (NCN) composites material for electrical conductive use are fabricated by a combination of gelcasting method and sintering under argon atmosphere. This paper describes a characterization of the NCN composites. On the surface and boundary of alumina particles, the NCN was homogeneously observed by SEM. High graphitization and a few defects on the graphite structure could be confirmed on the carbon structure analysis by Raman spectroscopy. The electrical conductivity shows the semiconductor like behavior depending on the defects in the carbon. Effect of the graphite structure on electrical conductivity was shown.

Key words: gelcasting, electrical conductivity, composite material, alumina, carbon

1. Introduction
Electrical conductive ceramics have been important technological applications especially for high advanced materials. The common method improving the electrical properties for an insulating ceramics would be by adding electrically conductive fillers such as metals [1], metallic oxides [2] or carbon. Recently, alumina and carbon-nanotubes (CNTs) composite have been reported [3-6]. Alumina materials are well known for its superior mechanical, thermal, chemical stability and electrical insulation property. While the CNTs, it has the high tensile strength, electrical conductivity and low density. According to some studies, the CNTs dispersion is very difficult because it has a strong attractive force of the van der Waals in each CNTs particle [7]. This will cause a segregation of fillers in composite materials. The segregated fillers will be cause the unwanted phase formation and anisotropy that results mechanical fragility and brittleness. There have been some studies to avoid those problems [3, 8].

In our group, we have been successful in fabrication of a composite ceramics of alumina matrix and nano-carbon network (NCN) by combination of gelcasting method [9] and sintering under inert atmosphere [10, 11]. By a role of the NCN as conductive fillers, this composite ceramics has good electrical conductivity. Scheme 1 shows a generation process of NCN. Monomer and cross-linker are homogeneously solved into the initial slurry as polymer network resources. The slurry is solidified to green body by polymerization reaction. The resultant polymer network exists uniformly between alumina particles. This polymer network is changed to the NCN with uniformity maintained through the sintering process. The uniformity of NCN is an advantage compared to other methods.

Properties of filler are important for properties of composite material. In previous work [11], the NCN was confirmed to graphite by transmission electron microscope analysis. But, other characterizations have not been investigated. In this paper, graphite structure and electrical conductivity of NCN is characterized

2. Experimental
2.1 Sample preparation
The composition of slurry used in this study is shown in table 1. Grade AL 160 SG-4 alumina powder (Showa Denko Co., Yokohama, Japan) was used. The mean particle size was 0.5 μm. An ammonium salt of polycarboxylate solution (Seruna D-305, Chukyo Yushi, Japan) was used as dispersant. Methacrylamide and N,N’-methylene-bis-acrylamide were used as an organic monomer and a cross-linker, respectively. Distilled water
was used for solvent. Ammonium persulfate was used in 10 mass% solution for an initiator. N,N,N',N'-tetramethyletylenediamine was used as a catalyst of polymerization.

Initial slurry was prepared by ball-milling for 24 hrs. Then the slurry was agitated under a vacuum condition for 15 min to degas. After mixing with the initiator solution and catalyst, the slurry was poured into a mold and kept quietly until solidification. The solidified wet green bodies were demolded and dried at 25 °C under controlled humidity from 90 % to 60 % for 5 days. The dried greenbody was sintered at 1700 °C for 2h under argon atmosphere.

2.2 Characterization

The cutting surface of the sintered sample was observed by scanning electron microscopy (SEM, JSM-7000F, JEOL, Japan). Electrical conductivity was measured by 4-probe method by using DC voltage current source/monitor (R6243, Advantest, Japan) under controlled ambient temperature from 0 °C to 50 °C. In this measurement, applied current was fixed to 0.1 mA then the voltage on the sample was measured.

Thermogravimetry from room temperature to 1000 °C (TG, TG-8120, Rigaku, Japan) was carried out to measure the carbon amount in the sintered sample. The heating rate was fixed to 5 °C per minute.

Raman spectroscopy for analysis of carbon contents in the sintered body was recorded over the frequency range 1000 – 2000 cm⁻¹ at an interval of 1.86 cm⁻¹ with collection time of 10s (Laser Raman Spectrometer NRS-3100, JASCO, Japan). A 532 nm laser beam of 11 mW was used as excitation source.

3. Results and Discussion

Figure 1 shows the SEM image of the cutting surface on the sintered sample. This observation was carried out without coating by conductive materials. Thus, this image indicates that each alumina particles were uniformly coated by the NCN and improved electrical conductivity. According to this image, tow shapes of the NCN was expected. One is a shell type shape surrounding alumina particles. And another is a fibrous shape on the boundary of particles.

Figure 2 shows the TG result of sintered sample. Total weight loss was 1.37 mass%. The result showed two stages of weight loss. The first occurs in the temperature from 250 °C to 450 °C. This weight loss is due to the vaporization of low molecular weight carbon contents. While the second weight loss around 500°C was 1.01 mass%. This temperature is similar to the combustion temperature of a general carbon material. Assuming the density of NCN is similar as graphite (2.25 g/cm³) and porosity of composite is 0, the volume ratio of the CNC is calculated to about 1.5 vol% in the sintered body.

In figure 3, the results of Raman spectroscopy of the sintered sample was shown. Two peaks at 1360 cm⁻¹ (D-band) and 1580 cm⁻¹ (G-band) were focused as a structural index [12, 13]. The intensity ratio of these two peaks (I₁₃₆₀/I₁₅₈₀) was used as an index of graphitization of the carbon. This value indicates the ratio of basal plane and edge side or defects of graphite structure. And the half band width of 1580cm⁻¹ peak (Δν₁₅₈₀) is used as a local graphitized completeness index. From the result, the value of I₁₃₆₀/I₁₅₈₀ was 0.32. This value indicates that a few defects are remained on the graphite structure of NCN. The Δν₁₅₈₀ was 24.1. These values are similar as the edge surface of pyrolytic graphite [14]. On the basal surface of high oriented pyrolitic graphite I₁₃₆₀/I₁₅₈₀ is 0 and Δν is 18. When a Glassy carbon heat treated at 2000 °C, I₁₃₆₀/I₁₅₈₀ is 1.22 and Δν is 64. Comparing to these general carbon materials, those values of the NCN show relatively high graphitization. Generally, fabrication process of graphite from polymer needs heat treatment at high temperature (such as 2000 – 3000 °C) and expanding to achieve the high graphitization [15]. However, NCN is not treated by such processes.

The electrical conductivity of sintered body was 3.49 S/cm at 25 °C. When the content volume of NCN is taken into consideration, this value is a high value. The electrical conductivity increased upon increasing the
ambient temperature as shown in Figure 4. This tendency was similar as semiconductor. Semiconductor like behavior of a carbon material was reported and interpreted as effect of the defect on a graphite structure [16]. It is thought that the defect on the NCN graphite structure confirmed by Raman analysis is the cause of this semiconductor behavior.

The general possibility for this mechanism of the graphitization would be the following. First, the gel polymer becomes very flexible in attaching into the alumina particles at the low temperature during sintering period. Perhaps, the shape of NCN was formed during this stage. Then, the polymer converted into a carbon by a thermal decomposition. But the mobility of the polymer will be restrained by the interaction with alumina particles. Hence, graphite planes would appear in the carbon and connects each other as network that will eventually surrounds on the particle surface. Finally, carbon contents take the graphite structure which will form as NCN. In such a graphitized generation process, whether the defect occurs in the part where the polymer chain is restrained by the interaction with particles. These defects would lead to semi conductive electrical properties for the fabricated composite sintered material.

4. Conclusion

Characterization of NCN in the alumina matrix fabricated by gelcasting method and sintering under inert atmosphere has been demonstrated. The nano carbon network (NCN) can be confirmed as a shell and fibrous materials as seen in SEM micrograph. Though did not do the process to improve the orientation such as high temperature heat treatment and expanding. The graphite structure is relatively high compared to the general carbon. Some structural defects occurred into the NCN. This character of graphite is appeared on the electrical conductivity behavior. It is confirmed that NCN leads to the electrically conductive for the fabricated material. Hence, possibility of controlling the NCN graphite structure should be investigated for further research works in gel cast composite alumina/NCN material.

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