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Formation of polyhedral graphite particles by high-density carbon arc discharge with ethanol vapor

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A B S T R A C T

Polyhedral graphite (PG) particles that have a structure composed of many polyhedra with 100 nm −1 μm diameters were formed by using a modified arc discharge method (high-density carbon arc discharge method). The high-density carbon arc discharge was maintained by pyrolysis of ethanol during sublimation of a carbon anode. In this study, we investigated the most effective conditions for forming PG particles in high-density carbon arc plasma with ethanol vapor. We found that diameters of PG particles depended on arc current and that PG particles were effectively formed by using the high-density carbon arc discharge method. Furthermore, results of heat treatment at 2000 °C indicated that the obtained PG particles were graphitized well and that surfaces of the particles with diameters over 400 nm tended to peel off. Compared with the conventional laser vaporization method, the newly developed high-density carbon arc discharge method does not require an expensive equipment and high-pressure atmosphere gas, and is easy to scale up for mass production of PG particles.

1. Introduction

Carbon particles have various structures and attractive properties and have been studied as promising basic materials [1,2]. Among them, polyhedral graphite (PG) particles that have a structure composed of many polyhedra with 100 nm −1 μm diameters are formed by laser-vaporizing graphite in a high-pressure Ar atmosphere [3]. PG particles are formed by irradiating a pure graphite target by using a millisecond-pulsed CO_2 laser in a high-pressure Ar atmosphere (0.8 MPa) at room temperature [4]. Powder X-ray diffraction (XRD) patterns of the PG particles show predominant peaks of the (100) and (101) reflections of graphite characterizing the turbostratic structure. An ellipsoidal shell about 5 nm in diameter is present at the center of a PG particle. PG particles have a closed shell structure with hundreds of graphite layers surrounding the shell. Because there are irregular splits and defects between the graphite layers, distortion appears radially in PG particles.

PG particles are expected to resist abrasion and can be used as a lubricant because of their unique structures and properties, such as chemical and mechanical stability during high-pressure compression. Nakayama et al. used XRD to investigate the crystal structure of PG particles pressurized from atmospheric pressure to 43 GPa at room temperature [5]. In the case of single-crystal graphite, phase transformation occurs in a hexagonal diamond at room temperature under a pressure of 14 GPa [6,7]. In contrast, the PG particles maintained the graphite layer even under pressurized conditions of more than 40 GPa. Under pressurized conditions of 43 GPa, volume was compressed by 29% and layer spacing was reduced by 25%. The PG particles recovered to the initial crystal structure when the pressure was released.

As mentioned above, the laser vaporization method is suitable for producing PG particles. This is because the formation of PG particles requires a reaction field of high temperature and high carbon density. In this respect, a high-temperature and high-carbon-density reaction field is relatively easy to achieve by setting the atmospheric gas to a high pressure ($>$ 0.8 MPa) in the laser vaporization method. However, the laser vaporization method is difficult to scale up due to limitations of laser equipment. On the other hand, the arc discharge method is easy to scale up for mass production, but a reaction field with high carbon density is difficult to form because arc plasma is not generated in high-pressure atmospheric gas.

Arc discharge has long been used to produce ultrafine particles and nanoparticles. Ueda reported that ultrafine particles such as iron, silicon, silicon carbide, and γ-Al_2O_3 were produced by arc discharge using oxide or carbide in an Ar atmosphere [8]. Zhong et al. reported that nanoparticles of 5–70 nm were formed by evaporating Ni or Co by direct arc discharge in a He atmosphere of 500 Torr [9]. Since the

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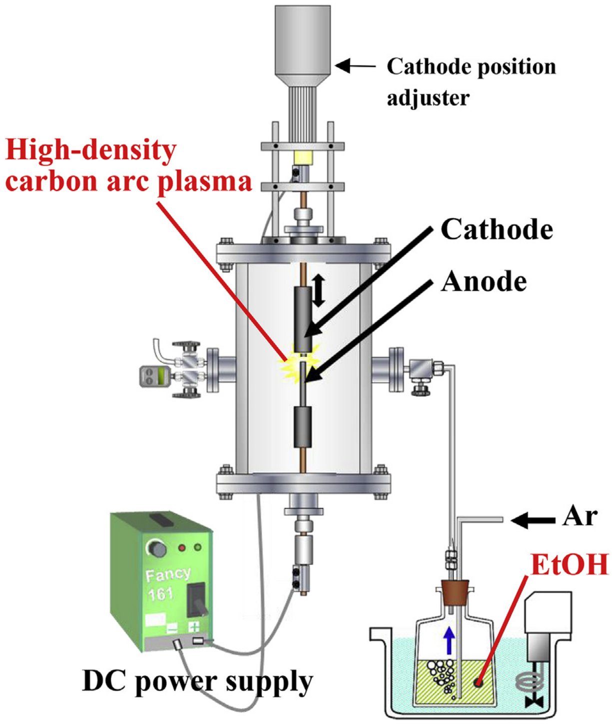

Fig. 1. Schematic diagram of high-density carbon arc discharge apparatus used in this study.

fullerene mass-production method was developed [10], arc discharge has been effectively utilized to fabricate various nanocarbon materials. In the general arc discharge method for forming nanocarbon materials, arc plasma is generated by separating two carbon electrodes by about 1–2 mm and flowing a large current between them. The arc plasma evaporates the carbon electrode of the anode, which becomes hotter. Metal and metal oxides contained in the anode can also be vaporized at the same time. Multi-walled carbon nanotubes were found in the cathode deposits obtained by arc discharge under an Ar gas atmosphere of 100 Torr [11], and thereafter it was soon reported that single-walled carbon nanotubes can be formed using a carbon electrode containing Fe, Co, or Ni as catalysts [12–14]. Furthermore, it has been reported that various nanocarbon materials such as high-purity carbon nanotubes [15] and carbon nanohorns [16] can be produced by using a modified arc discharge method. In addition to the arc discharge in the gas phase, various modified arc discharge methods have been reported to date, such as arc discharge in liquid [17–19] and arc discharge using AC power supply instead of DC power supply [20,21].

It is important to form large quantities of PG particles at a low cost with a simple method to apply the fruitful properties industrially to various materials. Arc discharge is one of the most feasible methods. In this study, to solve the problem of low carbon density in conventional carbon arc plasma, we have developed an arc discharge method that can achieve high carbon density by using ethanol vapor as an additional carbon source during conventional arc discharge. We have named the method “high-density carbon arc discharge.” We investigated the most effective conditions for forming PG particles by high-density carbon arc discharge using ethanol. In this paper, we report on changes in the diameter of PG particles dependent on arc current and changes in their structure caused by heat treatment.

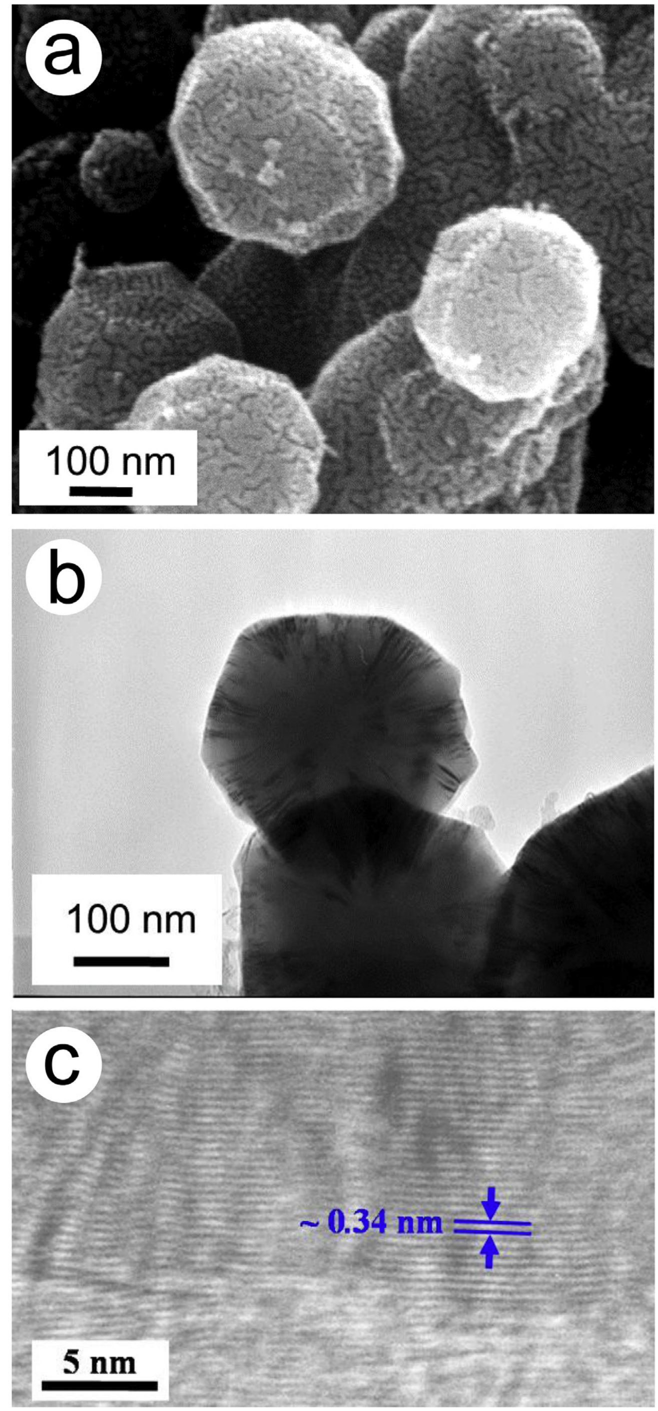

Fig. 2. (A) SEM and (b) TEM images of PG particles produced by high-density carbon arc discharge with ethanol vapor. (c) HR-TEM image of PG particle surface.

2. Experimental

The PG particles were produced by conventional DC arc discharge using carbon electrodes with ethanol vapor introduced into the arc plasma in an Ar atmosphere (Fig. 1). High-purity carbon rods (99.99%, Nilaco Corporation) were used as two electrodes: an anode of 5 mm in