Formation of Co filled carbon nanocapsules by metal-template graphitization of diamond nanoparticles

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Co filled carbon nanocapsules, which are formed by a heat treatment of the mixture of Co and diamond nanoparticles, have been studied by *in situ* transmission electron microscopy (TEM), x-ray diffraction, and Raman spectroscopy. Raman studies show that the heat treatment reduces the surface native oxide (Co_3O_4) of Co nanoparticles. The reduction is accompanied by graphitization of diamond nanoparticles, indicating that diamond nanoparticles being in contact with the metallic Co are transformed into graphitic coating. The *in situ* TEM studies show that the graphitic coating is formed in the heating process, not in the cooling process. Furthermore, once the coating is completed, the number of the graphitic layers is almost constant on further heating and cooling. These results allow us to conclude that metallic Co particles simply act as templates for graphitic coating. © *2000 American Institute of Physics.* [S0021-8979(00)07522-8]

I. INTRODUCTION

Metal nanoparticles wrapped in concentric layers of encapsulating graphitic carbon, called carbon nanocapsules, have been intensively studied since LaC_2 was successfully encapsulated.[1,2] Particularly for magnetic-metal filled carbon nanocapsules, the interesting magnetic behavior of magnetic-metal nanoparticles and the oxidation resistance of the carbon coating have led to the consideration of these particles for applications in areas such as magnetic data storage, magnetic tonor for xerography, fellofluids, and contrast agents in magnetic resonance imaging.[3] Graphitic coating increases the effective distance of neighboring magnetic particles.[4] The increase reduces particle–particles exchange coupling, which is an important issue in ongoing attempt to synthesize extremely high-density magnetic recording media.[5–7]

Magnetic-metal filled carbon nanocapsules have been produced by various methods via vapor phase reaction, e.g., standard arc methods,[8,9] modified arc methods,[4,10] and sputtering methods.[7,11,12] The nanocapsules are thought to be formed by so-called ''dissolution-precipitation mechanism,'' in which carbon is dissolved into the metal, and graphite precipitates as coating layers on quenching. Jiao and Seraphin[13] showed that, for the nanocapsules prepared by the modified arc discharge, the thickness of the coating increases by postannealing. They claimed that the addition of graphitic layers results from a precipitation of carbon previously dissolved in the metal, suggesting the dissolution-precipitation mechanism in these systems.

Very recently, we succeeded in preparing magnetic-metal filled carbon nanocapsules via solid-state reaction.[14] The method used is the heat treatment of the mixture of magnetic-metal nanoparticles about 30 nm in diameter and diamond nanoparticles about 5 nm in diameter. After the heat treatment at 1700 °C, all the magnetic-metal nanoparticles were encapsulated with uniform thin graphitic layers. The thickness of the coating was nearly the same as the diameter of the initial diamond nanoparticles. These results imply that diamond nanoparticles being in contact with the metals are transformed into the thin coating. However, there was no clearcut explanation for the detailed formation mechanism of the graphitic coating, although it was obvious that the formation is assisted by the magnetic-metals.

In this article, we intend to clarify the formation mechanism of Co filled carbon nanocapsules by *in situ* transmission electron microscopy (TEM), x-ray diffraction (XRD), and Raman spectroscopy. In the initial mixture, surface oxidized β-Co nanoparticles about 30 nm in diameter are surrounded by diamond nanoparticles about 5 nm in diameter. Raman study indicates that the surface native oxide (Co_3O_4) is reduced to metallic Co as the heat treatment temperature increases. The reduction is accompanied by the drastic

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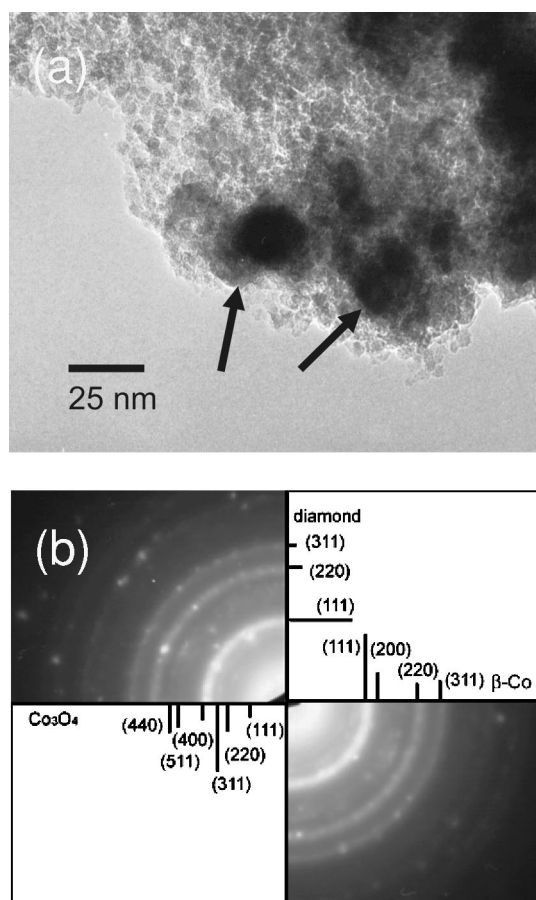
FIG. 1. A TEM image (a) and a SAED pattern (b) of the initial mixture of Co and diamond nanoparticles. Co nanoparticles about 30 nm in diameter (indicated by arrows) are surrounded by diamond nanoparticles about 5 nm in diameter.
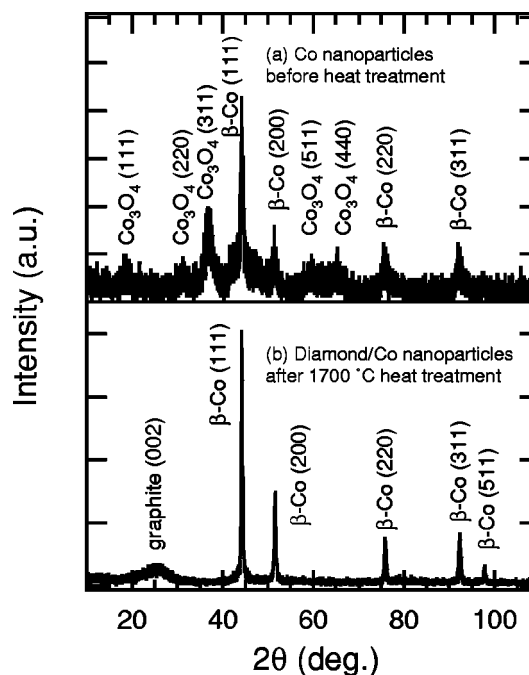

FIG. 2. XRD profiles of initial Co nanoparticles before heat treatment (a) and the mixture of Co and diamond nanoparticles after the heat treatment at 1700 °C (b).

progress of graphitization of diamond nanoparticles. The result supports our hypothesis that diamond nanoparticles being in contact with metallic Co are transformed into graphitic coating. *In situ* TEM experiments show that the graphitic coating is formed not on the cooling but on the heating process. Once the coating is completely formed, the number of the graphitic layers is almost constant on further heating and cooling. These results brought by *in situ* TEM studies cannot be explained within the framework of the dissolution-precipitation mechanism. We thus propose a metal-template graphitization mechanism, in which metallic Co particles simply act as templates for the coating.

II. EXPERIMENT

Co filled carbon nanocapsules were prepared by the heat treatment of the mixture of Co and diamond nanoparticles.[14] Diamond nanoparticles about 5 nm in diameter were mixed with Co nanoparticles about 30 nm in diameter using ultrasonic dispersion. Both of the nanoparticles were commercially available. The mixture was put in a hole (2.5 mm in diameter) which was drilled through a graphite rod (5 mm in diameter and 7 mm in length). The graphite rod was then heat treated at the temperatures ranging from 300 to 800 °C

in vacuum ($<2 \times 10^{-3}$ Pa) in a conventional electric furnace, and from 800 to 1700 °C by an electron beam irradiation in vacuum ($<2.5 \times 10^{-3}$ Pa).

TEM studies were performed with JEOL JEM-2010 and Hitachi HF-2000 transmission electron microscopes at an acceleration voltage of 200 kV. For the *in situ* observation, the sample was placed on a W filament, which was attached to the sample holder, and resistively heated. The temperature of the sample was roughly estimated from the current, which is supplied to a W filament, by using a calibration curve obtained from standard samples (Au). An XRD measurement was performed with an x-ray diffractometer [RINT-2100 (RIGAKU)] with the Cu K_{α} radiation. Raman spectroscopy was carried out with a SPEX 1877 Triplemate equipped with a charge coupled device. Spectra were recorded in a 90° scattering geometry. The excitation source was the 514.5 nm line of an Ar-ion laser. The excitation power was kept less than 10 mW in order to avoid local heating.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b), respectively, show a TEM image and a selected-area electron diffraction (SAED) pattern of the mixture of Co and diamond nanoparticles before the heat treatment. Figure 1(b) also exhibits diffraction patterns calculated from the American Society for Testing and Materials data[15] for β-Co with a fcc structure, Co_3O_4 and diamond; the length of the bars represents diffraction intensity. The SAED pattern indicates that the initial mixture consists of β-Co, Co_3O_4, and diamond. Co_3O_4 is a native oxide formed on the surface of Co nanoparticles.[16] The presence of Co_3O_4 as well as β-Co in the initial Co nanoparticles is also confirmed by an XRD study as shown in Fig. 2(a). Therefore, dark patches in Fig. 1(a) (indicated by arrows) correspond to β-Co nano-
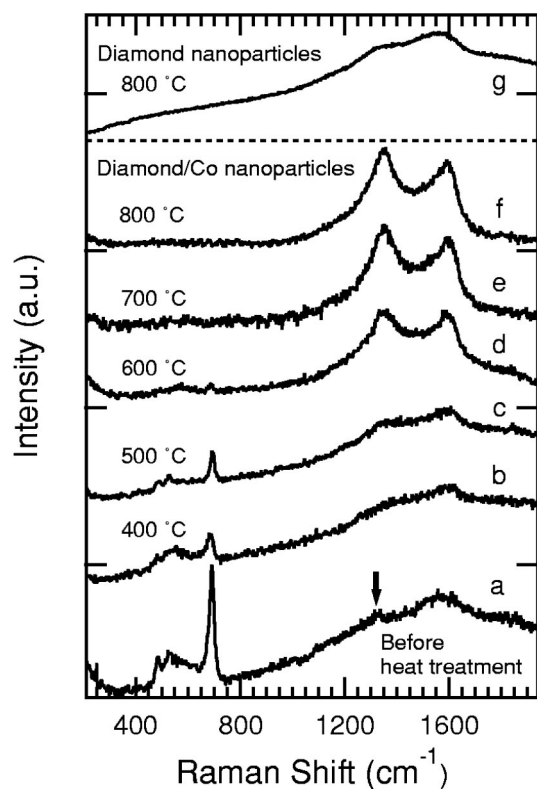
FIG. 3. Raman spectra obtained from initial mixture (curve a) and samples with different heat treatment temperatures (curves b–f). The top curve g represents a Raman spectrum of the diamond nanoparticles heat treated at 800 °C without Co nanoparticles.

FIG. 4. A typical TEM image of a graphitic-carbon encapsulated Co nanoparticles formed after heat treatment at 1700 °C.

particles with surface oxides, and the surroundings are diamond nanoparticles about 5 nm in diameter. The fcc structure is the high temperature phase for Co and normally presents only above 420 °C. The presence of the high temperature phase at room temperature is probably due to the small particle nature of the material and/or ''quenching'' effects.[17]

Figure 3 shows the heat treatment temperature dependence of Raman spectra. Before heat treatment (curve a), the spectrum exhibits a weak Raman band at about 1325 cm^{-1} which originates from diamond nanoparticles (indicated by an arrow). The band is slightly shifted toward a lower frequency compared with that for the bulk diamond (1332 cm^{-1}). This shift is explained by the phonon confinement effects.[18–20] In addition to the diamond band, a broad band can be seen at a higher wave number region. The broad band is thought to originate from the surface amorphous carbon layers of the diamond nanoparticles.[20,21] The spectrum a also shows three Raman bands at about 483, 523, and 691 cm^{-1}. These bands are attributed to Co_3O_4.[22]

The carbon-related features above 1200 cm^{-1} do not change up to the heat treatment temperature of 500 °C (curves b and c). In contrast, the Co_3O_4 bands become weaker, suggesting that Co_3O_4 is reduced to metallic Co with increasing the heat treatment temperature. The Co_3O_4 bands almost disappear at 600 °C (curve d). Since Co_3O_4 is normally stable up to 600 °C, diamond nanoparticles may act as a reducing agent. We confirmed the reduction of Co_3O_4
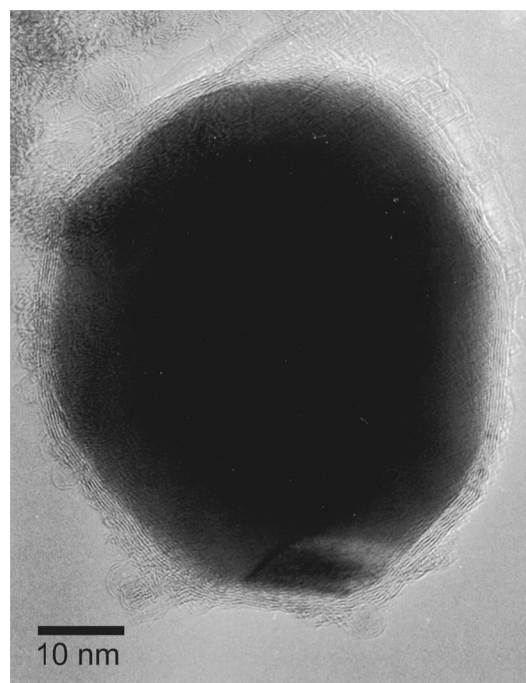
also by differential scanning calorimetry, which shows a endothermic peak around 600 °C.

The disappearance of Co_3O_4 bands at 600 °C is accompanied by the drastic change in carbon-related features; the band due to the graphitic structure (*G* band) at about 1580 cm^{-1} and disorder-induced band (called *D* band) at about 1350 cm^{-1} emerge. This implies that when the reduction of Co_3O_4 is completed, the graphitization of diamond nanoparticles starts. The reduction of surface Co_3O_4 layers allows diamond nanoparticles to directly contact with metallic Co particles. The direct contact enables diamond nanoparticles to be transformed into graphitic coating owing to the catalytic effect of metallic Co for graphitization.[23,24] The top curve g in Fig. 3 represents a spectrum of the diamond nanoparticles annealed at 800 °C without mixing with Co particles. The carbon-related features are smeared and very similar to those in curves b and c, suggesting that, without Co nanoparticles, graphitization does not proceed even at 800 °C.

Figure 4 shows a TEM image for the sample heat treated at 1700 °C. A nanocapsule about 65 nm in diameter with thin coating can be seen. The spacing of the lattice fringes of the coating is around 0.34 nm, which is close to that of the graphite (002) planes. The thickness of the coating is nearly the same as the average diameter of diamond nanoparticles. XRD profile [Fig. 2(b)] shows the presence of graphitic carbon and β-Co. Neither carbide nor oxide phase is found in the profile. Although not shown here, the TEM observation indicated that the graphitic coating starts at about 600 °C.

The results of TEM, SAED, XRD, and Raman studies revealed that diamond nanoparticles being in contact with metallic Co are transformed into graphitic coating, resulting in the formation of Co filled carbon nanocapsules. Neverthe-
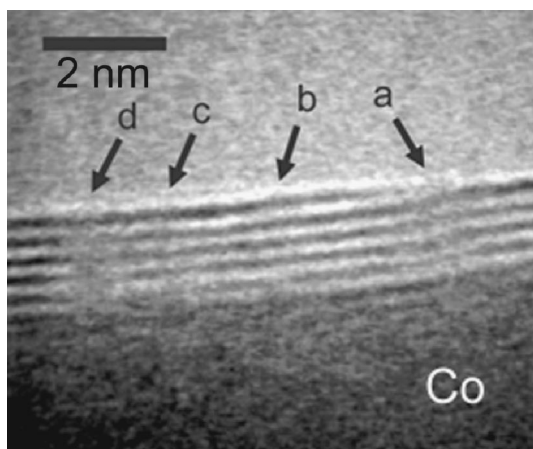
FIG. 5. The *in situ* TEM image of the coating on heating process. The coating consists of 6 or 7 graphitic layers. The micrograph also shows defects as indicated by arrows a, b, c, and d.

less, the formation mechanism of the graphitic coating, particularly the role of metallic Co, is still unclear. In order to gain more detailed information about the formation mechanism, we performed *in situ* TEM experiments.

The initial mixture was put into the microscope and the sample temperature was gradually increased by increasing the current supplied to a W filament (heating process). The lattice fringes due to Co oxide disappeared above 600 °C, and then the graphitic coating of the nanocapsules is formed. Figure 5 shows an *in situ* TEM image of a part of the coating during the heating process. The temperature of the sample was estimated to be about 1100 °C. Clear lattice fringes corresponding to (002) planes of graphite can be seen. The coating consists of 6 or 7 graphitic layers and is about 2 nm in thickness. Once the coating was completely formed, the number of graphitic layers was found to be almost constant on further heating. Figure 5 also shows that the coating has defects as indicated by arrows a, b, c, and d.

After heating up to 1100 °C, we gradually decreased the sample temperature by decreasing the current (cooling process). Upon cooling, Fig. 6 was obtained at the same place as

in Fig. 5; the point *a'* is the same place as the point a in Fig. 5. Note here that the number of the layers on cooling is almost the same as that on heating. However, the crystallinity of the graphitic coating is much different. The coating becomes disordered and is similar to turbostratic carbon that is made up of small segments of graphitic sheets stacked roughly parallel to the particle surface. The disorder is thought to be induced by the different heat-expansion coefficient between Co and graphite.

From these results of *in situ* TEM experiments, we will discuss here the formation mechanism of the graphitic coating and the role of metallic Co. It is obvious that the transformation of diamond nanoparticles into graphitic coating is assisted by the Co nanoparticles. Catalytic effects by the metals in graphitization have been investigated for some decades.[23–25] Sinclair and co-workers[26–28] showed that amorphous carbon in contact with Co fully crystallizes between 500 and 600 °C. This graphitization temperature is close to the present result; present Raman study indicates that diamond nanoparticles are graphitized at about 600 °C. They suggested a model of metal-mediated graphitization, in which carbon is dissolved into the metal, and upon supersaturation, graphite precipitates outwardly at the interface, just similar to the dissolution-precipitation mechanism. However, as depicted in a binary alloy phase diagram,[29] the equilibrium solubility of carbon in Co at 600 °C is extremely low (about 0.2 at. %); the carbon does not dissolve into Co. Therefore, there has been ambiguity whether or not graphitization at 600 °C is really mediated by the dissolution of carbon atoms into the interstitial and/or substitutional sites in metallic Co.

For the nanocapsules prepared by modified arc discharge method,[13] the thickness of the coating increased by postannealing, suggesting that the addition of graphitic layers results from a precipitation of carbon previously dissolved in the metal. This is thought to be an evidence of dissolution-precipitation mechanism. On the contrary, present TEM studies show that, once the coating is formed, the number of the graphitic layers does not increase on further heating and cooling. The present formation mechanism is thus different from the dissolution-precipitation mechanism. In other words, diamond nanoparticles are not dissolved into Co nanoparticles but directly transformed into the graphitic coating on the surface of Co. It is likely that the surface of metallic Co provides a fast path to release the excess free energy of diamond nanoparticles[30] and a medium for the diffusion of mobile carbon atoms,[31] thus facilitating crystalline growth of graphitic layers. As a conclusion, we suggest that the present formation mechanism of Co filled carbon nanocapsules is a metal-template graphitization, in which metallic Co simply acts as templates for the coating.

IV. CONCLUSION

The formation of Co filled carbon nanocapsules has been studied by *in situ* TEM, XRD and Raman spectroscopy. In the initial mixture, surface-oxidized β-Co nanoparticles about 30 nm in diameter were surrounded by diamond nanoparticles about 5 nm in diameter. Raman studies showed that
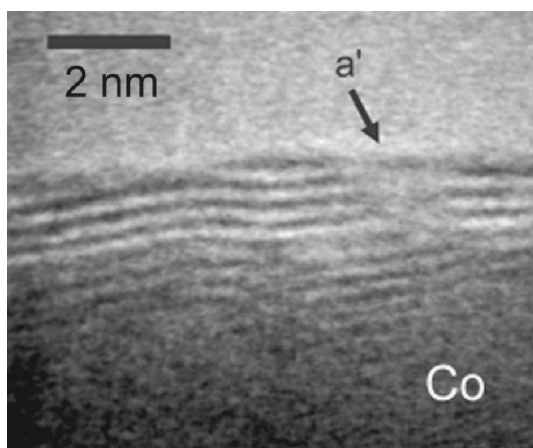

FIG. 6. The *in situ* TEM image on cooling process at the same place as in Fig. 5. Note that the number of the layers on cooling is almost the same as that on heating although the crystallinity is much different.

the reduction of Co_3O_4 to metallic Co at about 600 °C is accompanied by the drastic progress of graphitization of diamond nanoparticles, suggesting that diamond nanoparticles being in contact with the metallic Co are transformed to the graphitic coating layers. *In situ* TEM experiments showed that the graphitic coating is formed not on cooling but on heating process. Moreover, once the coating was formed, the number of the graphitic layers was almost constant on further heating and cooling. These results allow us to conclude that metallic Co simply acts as templates for the formation of the graphitic coating (a metal-template graphitization mechanism). Metallic Co particles provide the place to release the excess free energy of diamond nanoparticles and diamond nanoparticles are recrystallized as graphitic coating layers on the surface of Co.

ACKNOWLEDGMENTS

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