DEVELOPMENT OF LOW-CURRENT PLASMA PROCESS WITH ULTRASONIC CAVITATIONS FOR SYNTHESIZING METAL-FILLED CARBON NANOCAPSULES IN ORGANIC SOLUTION

Ruslan Sergiienko, Etsuro Shibata, Takashi Nakamura
IMRAM, Tohoku University, 1, 1 Katahira, 2 Chome, Aobaku, Sendai 980-8577, Japan

Introduction

The magnetic nanoparticles of 3d metals (iron, nickel, and cobalt) coated with graphite shells are of considerable interest owing to their potential applications in magnetic ferrofluids [1], magnetic recording materials [2], biomedicine (transport of anticancer drugs, contrast enhancement of magnetic resonance imaging (MRI)) [3] and other applications. The nanometer-sized particles readily oxidize upon exposure to air. One approach to chemical stabilization is the formation of protective shell around the nanoparticle surface which thus prevents the reaction of oxygen with the surface atoms. The graphitic carbon shell protects effectively against environmental degradation and has excellent adhesive bonding with the surface of the metal particles. Such graphitic carbon shells are airtight and protect the entrapped materials from oxidation, and they are generally known as "carbon nanocapsules" (CNCs).
Carbon nanocapsules are usually synthesized by a conventional and modified arc discharge with a composite carbon rod anode or graphite crucible anode (containing metal or metal oxide precursors) [4, 5]. However, neither the conventional nor modified arc discharge method can be applied without expensive vacuum equipment; the power required by the arc discharge usually exceeds 1 kW.
In presented here method an electric plasma discharge could be generated in an organic liquid under ultrasonic irradiation at a remarkably low DC voltage, current, such as 55 V, 3A, respectively. The developed method was applied to synthesize iron and cobalt carbide-filled carbon nanocapsules.

Experimental

Synthesis
The scheme of the experimental apparatus for the synthesis of metal-filled carbon nanocapsules in liquid ethanol is presented in Fig. 1. Low-current plasma discharge was generated between the metal anode (ø 3 mm, purities of Fe and Co anodes were 99.9%) and the bottom of the ultrasonic tip cathode (ø 18 mm, made from Fe or Co same purity as electrode anode) fixed on the top of a titanium ultrasonic horn.
Ultrasonic cavitation bubbles were induced between the gap of cathode and anode electrodes in the liquid ethanol. An ultrasonic homogenizer (Nissei, US-600NCVP) was used at 600 W and 20 kHz in the experiments to irradiate 300 ml of liquid ethanol (Wako, S-grade). During an ultrasonic irradiation, the voltage between the electrode-anode and ultrasonic horn was kept at 55 V using a regulated DC power supply (PAS 60-18), and the limit current of the power unit was set at 3.0 A.

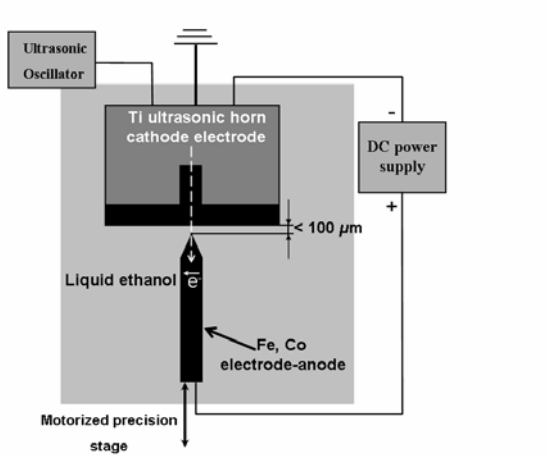

Fig. 1. Scheme of the experimental apparatus.

Treatment and characterization of carbon nanocapsules
After plasma discharge experiment, the produced carbonaceous powder dispersed in liquid ethanol was separated by centrifugation from remaining liquid ethanol using a centrifuge (Kobuta 6200) at 4000 rpm for 10 min. The resulting centrifuged powder was then etched in a 15 % HCl solution for 24 h at 313 K to remove insufficiently encapsulated metal nanoparticles and oxides. After drying in a vacuum at 313 K, the carbon powder samples were annealed in an argon-hydrogen gas mixture (Ar+3%H_2) at different temperatures (573-1173K) for 1-2 h.
The morphologies and structures of the carbon nanocapsules were characterized using a transmission electron microscopy (TEM) (JEOL-3010), X-ray diffraction apparatus (XRD; Rigaku, RINT2000). A vibration sample magnetometer (VSM) operating at room temperature with an applied magnetic field ±1200 kAm^{-1} was used to measure the magnetic properties of the as-prepared and annealed powder samples.

Results and discussion

TEM investigations
Typical morphologies of the as-prepared iron and cobalt carbide-filled carbon nanocapsules carbon nanocapsules were shown in an earlier [6, 7] articles. The crystalline carbide (orthorhombic Fe_3C and monoclinic χ-$Fe_{2.5}C$ structures) cores are spherical in shape and covered with graphite layers. During the

analysis, spherical carbon nanocapsules with amorphous cores were also found in the as-prepared samples. At temperature 873 K, the iron carbides were almost completely transformed into the α-Fe phase and graphitic carbon, though majority of small-sized cores of CNCs (< 10-20 nm in size) remained as cementite. Figures 2a, b show the TEM image and corresponding selected-area electron diffraction pattern of a typical metallic iron nanoparticle covered with graphitic carbon after annealing at 873 K.

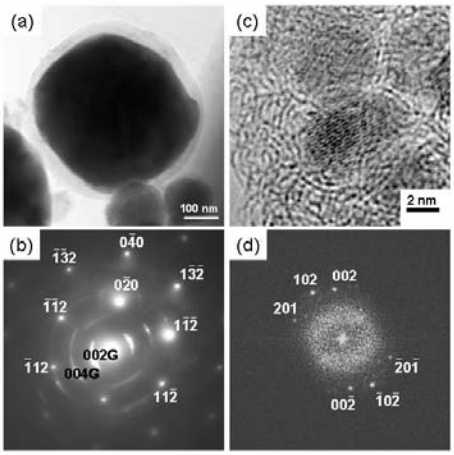

Fig. 2. (a) TEM image of an α-Fe particle and (b) the corresponding SAED from the core of α-Fe annealed at 873 K; (c) HRTEM image, and (d) the corresponding digital diffractogram computed by FFT of the cementite nanoparticle annealed at 873 K.

HRTEM observation of the annealed Co-filled CNCs revealed that the cobalt nanoparticles had existed both in the fcc (β-Co) and hcp (α-Co) forms. Figure 3a shows a HRTEM image of cobalt nanoparticles encapsulated in graphite-like carbon annealed at 873 K. The average diameter of the uniformly dispersed cobalt cores was estimated to be about 5 nm, with a fairly narrow size distribution (having a standard deviation of 1.1 nm).

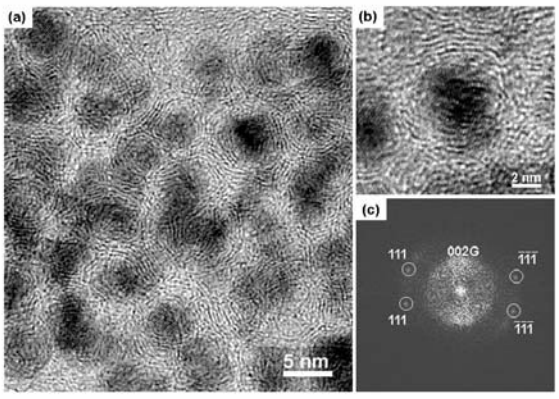

Figure 3. (a) HRTEM image of cobalt nanoparticles encapsulated in graphite shells annealed at 873 K; (b) magnified image of typical carbon nanocapsule and (c) digital diffractogram of carbon nanocapsule presented in (b) showing fcc β-Co spacings.

Magnetic properties of carbon nanocapsules

Whole samples showed a ferromagnetic behavior, attaining saturation at field ±1200 kAm^{-1}. The saturation magnetization, M_s, and coercivity, H_c, of the reference powders and all samples are summarized in Table 1 as a function of annealing temperature. The dependence of magnetic parameters on the annealing temperature is attributed to the change in the particle structure and composition, as well as to the particles' size and their morphology.

Table 1 Magnetic properties of synthesized metal-filled carbon nanocapsules

Samples annealed at temperatures, (K)	Saturation magnetization M_s, (Am^2kg^{-1})	Coercivity H_c, (kAm^{-1})
Iron-filled carbon nanocapsules		
As-prepared	48.0	4.16
673	65.5	10.90
873	80.6	9.36
1173	71.7	10.64
Cobalt-filled carbon nanocapsules		
As-prepared	24.22	5.17
733	49.15	15.50
873	51.04	15.50

Conclusions

Carbon-encapsulated metal carbide (Fe_3C, χ-$Fe_{2.5}C$, Co_3C, CoC_x) nanocapsules have been synthesized by low-current plasma processing in which ultrasonic cavitation permits an electric plasma discharge to occur at low levels of electric power. TEM measurements showed that the cores of the as-prepared carbon nanocapsules were composed of metal carbides with different size. Whole samples showed a ferromagnetic behavior, attaining saturation at ±1200 kA/m.

References

1. Odenbach, S. *J. Phys.: Condens. Matter.*, **16** (2004) R1135–R1150.
2. Hanayama, M and Ideno, T. Magnetic Recording Medium. Jpn Patent JP 06-152793.
3. Tartaj, P., Morales, M.P., Veintemillas-Verdaguer, S., González-Carreño, T., and Serna, C.J. *J. Phys. D: Appl. Phys.*, **36** (2003) R182-R197.
4. Saito, Y., and Masuda, M. *Jpn. J. Appl. Phys.*, **34** (1995) 5594-5598.
5. Jiao, J., Seraphin, S., Wang, X., and Withers, J.C. *J. Appl. Phys*, **80** (1996) 103-108.
6. Sergiienko, R., Shibata, E., Akase, Z., Suwa, H., Shindo, D., and Nakamura, T., *J. Mater. Res.*, **21(10)** (2006) 2524-2533.
7. Sergiienko, R., Shibata, E., Akase, Z., Shindo, D., Nakamura, T., and Qin, G., *Acta Materialia*, **55** (2007) 3671-3680.