

Research Article

Synthesis and Magnetic Properties of Ni and Carbon Coated Ni by Levitational Gas Condensation (LGC)

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The nickel (Ni), and carbon coated nickel (Ni@C) nanoparticles were synthesized by levitational gas condensation (LGC) methods using a micron powder feeding (MPF) system. Both metal and carbon coated metal nano powders include a magnetic ordered phase. The synthesis by LGC yields spherical particles with a large coercivity. The abnormal initial magnetization curve for Ni indicates a non-collinear magnetic structure between the core and surface layer of the particles. The carbon coated particles had a core structure diameter at and below 10 nm and were covered by 2-3 nm thin carbon layers. The hysteresis loop of the as-prepared Ni@Cs materials with unsaturated magnetization shows a superparamagnetic state at room temperature.

1. Introduction

Nanoparticles have achieved significant attention owing to the novel electro-optic, magnetic, and catalytic properties that arise from the quantum size effect and large specific surface areas that are characteristic of nanosized species [1, 2]. Magnetic nanoparticles have attracted much of the attention these days, because of their potential technological applications in nanofluids for biomedical application, thermal conductive fluids, various catalysts, and so forth [1–3]. However, the preparation of nanofluids using pure metal nanoparticles is very hard, because nanoparticles are inherently vulnerable to oxidation, dissolution and agglomeration. In particular, agglomeration of the particles in a solvent is a serious problem when preparing nanofluids. To overcome these problems, a protective shell has been recommended to improve the chemical stability of metal nanoparticles and the dispersion stability in the solvent [4–6]. It is also worth noting that these materials are not prone to agglomeration owing to the fact that the addition of a carbon coating layer reduces the magnetic interaction. In addition, the surface diffusion processes allow the preservation of the chemical and structural properties of the nanopowder for

a long time in many chemically aggressive surroundings [7]. In particular, a graphitic carbon shell is regarded as an ideal coating as it is light and shows high stability in both chemical and physical environments [8, 9]. The stable dispersion of nanoparticles in both aqueous and nonaqueous media has important applications in cosmetics, chemicals, pharmaceuticals, microelectronics, paints, and pigments [10, 11]. Nanoparticle dispersion depends on many factors, such as the solvent, pH, added ion, dispersant, and particle size. In particular, the preparation of a stable suspension of metallic nanoparticles is difficult owing to the high density and agglomeration of particles. Carbon-encapsulated metal nanoparticles are expected to have a large advantage for preventing the coalescence of the particles in the fluid. In this study, we introduce Ni and carbon-coated Ni (Ni@C) nanoparticles synthesized using LGC [11]. We also report on the dispersion stability in various solutions, such as water, ethanol, and ethylene glycol.

2. Experiment

High purity Ni and Ni@C nanopowders were synthesized by a LGC method using a micron powder feeding (MPF) system

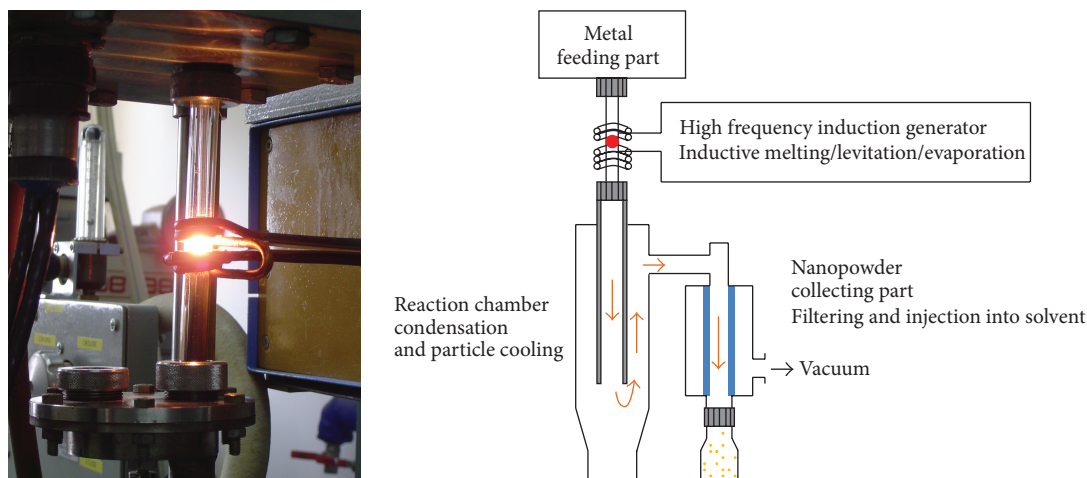


FIGURE 1: The shape of inductor and the concept of system for LGC.

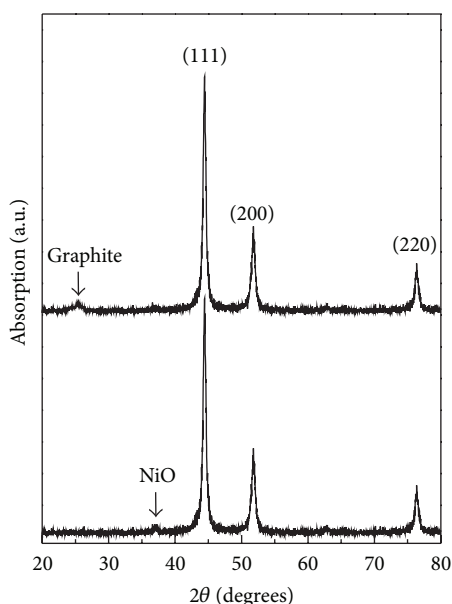


FIGURE 2: X-ray diffraction patterns for the Ni and Ni@C nanoparticles.

[11]. The apparatus consists of a high-frequency induction generator of 6 kW, a levitation and evaporation chamber, and a methane (CH_4) concentration control unit. Ni powder (99.9 at.%, $\sim 500 \mu\text{m}$) was used as a starting material for the synthesis of carbon encapsulated Ni nanoparticles. The Ni powders were mixed into the micron powder feeding system consisting of a rotation part for supplying the Ni micron powders to the melted droplet and a vibrating part for protecting the aggregation of the powder. The Ni micron powders were fed into a powder feeding system with the feeding rate of 80 mg/min. A Ni ingot of 87 mg, as a seed material for levitation and evaporation reactions, was melted by electric induction heat. The gas pressure for the Ar in chamber was 100 torr. The ratio of CH_4 was 10% of the mixture gas, when the carbon coated Ni was prepared.

The as-prepared sample was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and a vibrating sample magnetometer (VSM). The suspensions of Ni@C nanoparticles were prepared as follows: we prepared solvents of ethanol and polyethylene glycol (MW 20000) in 100 mL; we then added 0.01 wt.% of nanoparticles and ultrasonicated the suspension for 20 min. To characterize the dispersion stability, we used Turbiscan Lab. and took measurements every 1 hour for 3 days.

3. Results and Discussion

The Ni and Ni@Cs materials were obtained using the LGC. A liquid droplet which is levitated by the magnetic force acted against the gravitational force from the coupled induction coils. The induction heat coil and the concept of LGC system are displayed at Figure 1. The inductor is heated up to 2000°C and the metallic atoms evaporated from the overheated surface of the liquid droplet and condensed by cold inert gas and then collected into the filter [11]. The mechanism for the formation of Ni nanoparticles is evaporation and condensation. At the same time, the molecular CH_4 introduced into the chamber is converted into atomic C and H with high activity under high temperature. The highly active C atoms can react with Ni atoms. The H atoms converted into H_2 molecules. The newly created H_2 gas is vented out of the reaction chamber by continuous vacuum operation. The mechanism for the formation of graphitic carbon shell is reaction between active C atom and metal without chemical compounds of carbides [12].

Nanoparticles Ni and Ni@C synthesized by LGC using a micron powder feeding system were confirmed by an XRD pattern, as shown in Figure 2. The XRD results for Ni shows lattice parameters and the position of the main peaks of the Ni powders. The small amount of NiO phase was found in the XRD patterns and in the TEM images, which results from a passivation on the powder surface. The microstructure and phase composition of Ni powders were studied using TEM. A particle consists of a single domain. The powders with

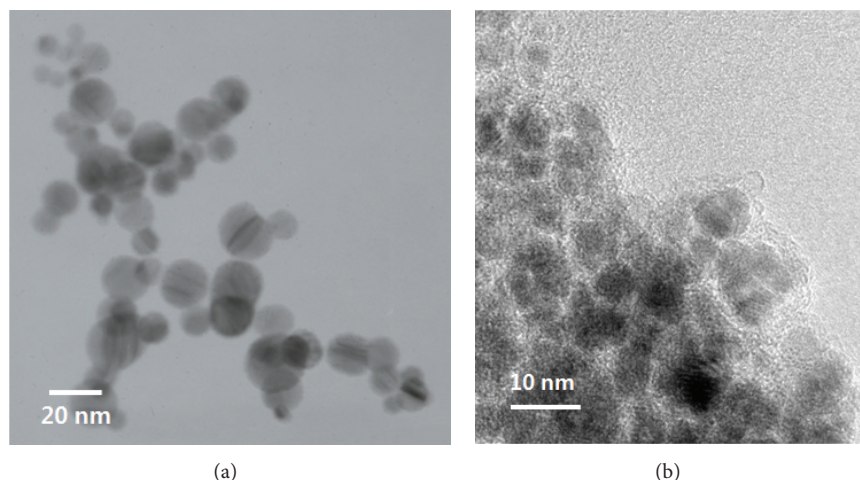


FIGURE 3: TEM images of (a) the Ni and (b) the Ni@C nanoparticles.

single domains are synthesized by a special gas phase method, though the average particle size is over 100 nm [12]. The thin oxide layer on powders forms a continuous coating with a thickness of 2–3 nm. Figure 2(b) shows the XRD patterns of the as-obtained Ni@C. All the main reflection peaks can be indexed to Ni. The strong nature of the peaks indicates that the final products are well crystallized and have high purity. The case of Ni@Cs materials is due to the (0 0 2) diffraction of graphite layers. However, the intensity for the (0 0 2) peak of the sample is broad and low. The shell layer in the Ni@Cs samples is made of amorphous carbon. For the Ni@Cs material, the diffraction peaks at 44.4° , 51.8° , and 76.3° are due to the (1 1 1), (2 0 0), and (2 2 0) planes of fcc-Ni, respectively.

The carbon shell structure of the Ni@Cs samples, which is further confirmed by the TEM results, is discussed in Figure 3. Nanoparticles Ni and Ni@C synthesized by LGC show a spherical shape as shown in Figure 3. The TEM image shows that nanocrystalline Ni powders consist of particles with the size ranges from 15 nm to 40 nm. The magnetic properties of nanopowders were affected by the size effect resulting from the anisotropy field and magnetic domain effect on the particles [13]. The morphologies of the carbon-coated Ni nanocrystallites were characterized by TEM as shown in Figure 3(b). The results indicated that all of the as-made materials were composed of only nanocapsules with a uniform particle size at and below 10 nm. At the previous study, nanocapsules consisted of outer multishells of carbon were observed using a high resolution TEM [13].

The powders synthesized by LGC method show low saturation magnetization for Ni. This results from a spin-canting effect and oxide phase on the surface [11]. The magnetic properties would be weak due to antiferromagnetic NiO phase on the powder surface. The saturation magnetization is $M_s = 42 \text{ emu/g}$. In Figure 4(a), the hysteresis loop of Ni in the low fields is shown. The slightly shifted hysteresis loop for the Ni sample can be explained by exchange bias between the ferromagnetic core of Ni and antiferromagnetic surface of NiO [12, 14]. The initial magnetization curve is not explained by the size effect. At previous studies, the

virgin magnetization curve slightly spills over the limited hysteresis loop at 655 Oe [13]. We assume that this effect enhances when the size of the particles is reduced, at previous study. With a decreasing particle size, the defects and the different magnetic structure on the surface of the particles are increased [13]. The nature of this irreversibility in high magnetic fields allows for the description of a physical model [12, 13]. This irreversibility can be explained by a spin-glass or spin-canting behavior. The VSM magnetic measurement results for the synthesized Ni@Cs materials are shown in Figure 4(b). The hysteresis loop of the as-made M@Cs materials in the magnetic field up to 1 T reveals the intrinsic magnetic behaviour, indicated by the magnetization (M), the remanent magnetization (M_r) and the coercive force (H_c) for the M@Cs samples (Figure 4(b)). The saturation magnetization demonstrated that the carbon-coated Ni nanocrystallites exhibited a superparamagnetic behaviour at room temperature. The magnetization was not saturated in the applied field up to 2 T as shown in Figure 4(c). The size of the nanoparticles may affect the value of the coercive field due to the size influence of the magnetization of the nanoparticles [13, 14]. In the case of very small nanoparticles one can observe superparamagnetic behaviour, related to the demagnetization effect arising from the additional energy of the magnetic fields outside the graphitic carbon encapsulation. The coercive force (H_c) and magnetization (M) were 76.6 Oe and 19.6 (emu/g), respectively. The ratio of remanence to the saturation magnetization (M_r/M) of the Ni@Cs samples is 0.04. The low magnetization comparing with the Ni nanoparticles without carbon-shell results in the coexistence of nonmagnetic carbon and a large surface spin percentage with disordered magnetization orientation for the nanoparticles [14, 15]. The magnetization and coercive force for Ni and Ni@C nanoparticles were influenced by both the particle size and the surface status on the particle.

To evaluate the dispersion stability and agglomeration phenomena of the carbon encapsulated Ni nanoparticles in solvents of ethanol and polyethylene glycol (PEG), the time-dependent sedimentation behavior was investigated by the

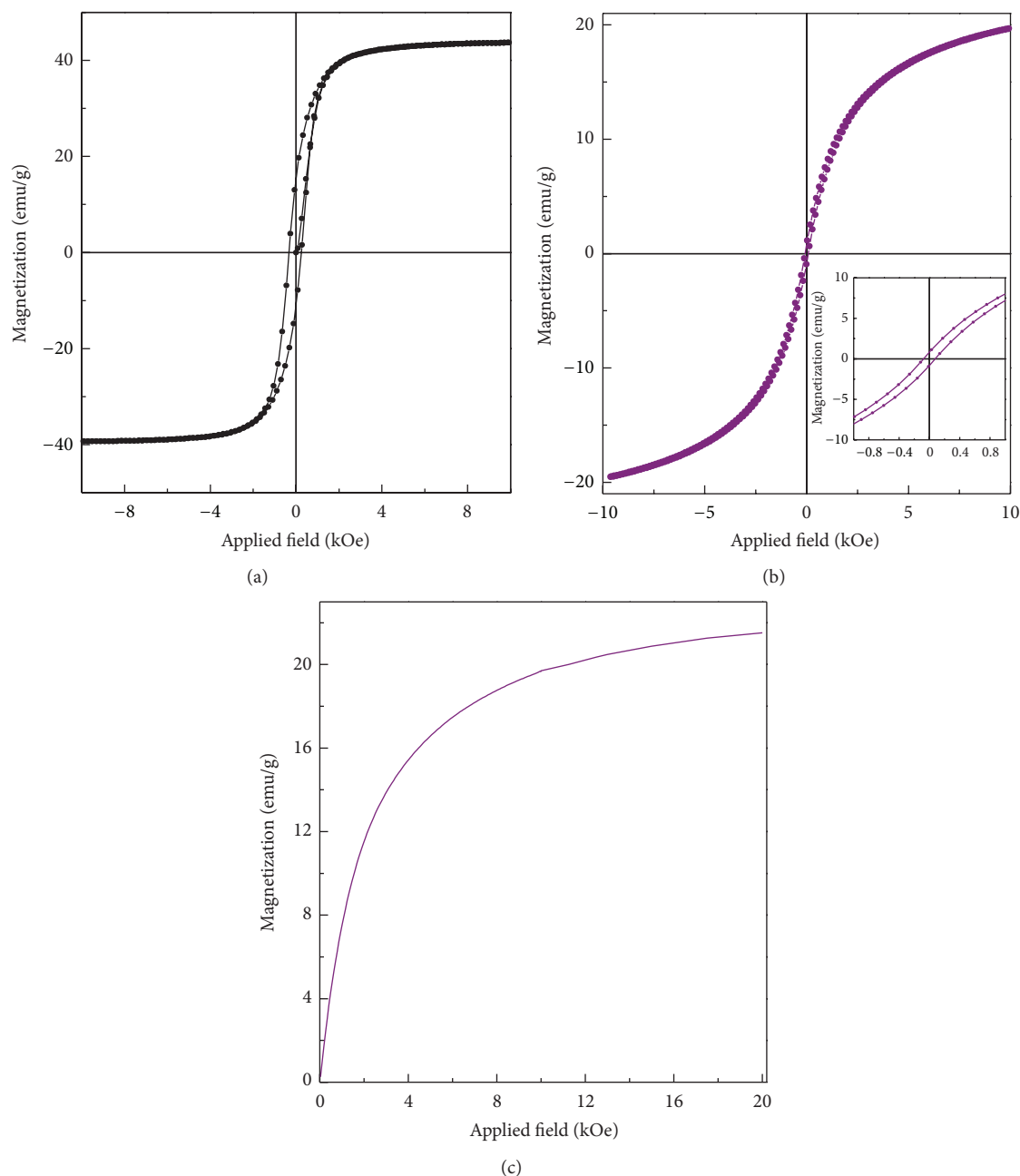


FIGURE 4: The hysteresis loops of (a) Ni and (b) Ni@C nanoparticles at room temperature. (Magnification of hysteresis loop for Ni@C is represented.) (c) Initial magnetization curve for Ni@C nanoparticles at room temperature.

transmission profile measurements using a Turbiscan Lab. The transmission profiles were taken every 1 hr for 72 hrs when the suspending medium was ethyl alcohol. It was found that the transmission intensity decreased at the sample top owing to a clarification and increased at the sample bottom from sedimentation, as shown in Figure 5 (a2) and (b2). A very stable Ni@C dispersion was observed without showing any clarification or sedimentation, as shown in Figure 5 (a1) and (b1). On the contrary, a progressive fall of the signal, which was observed as a function of time in the middle region of the Ni nanoparticles with an average particle size of 20 nm,

can be explained by flocculation-induced particle growth as shown in Figure 5 (a2) and (b2).

4. Conclusions

Nanoparticles Ni and carbon coated Ni were prepared by LGC. A simple approach to fabricate a carbon-shell layer is to use methane (CH_4) gas as the carbon source. The particle size of carbon-coated Ni with diameters in the range of up to 10 nm was smaller than those of Ni nanoparticles

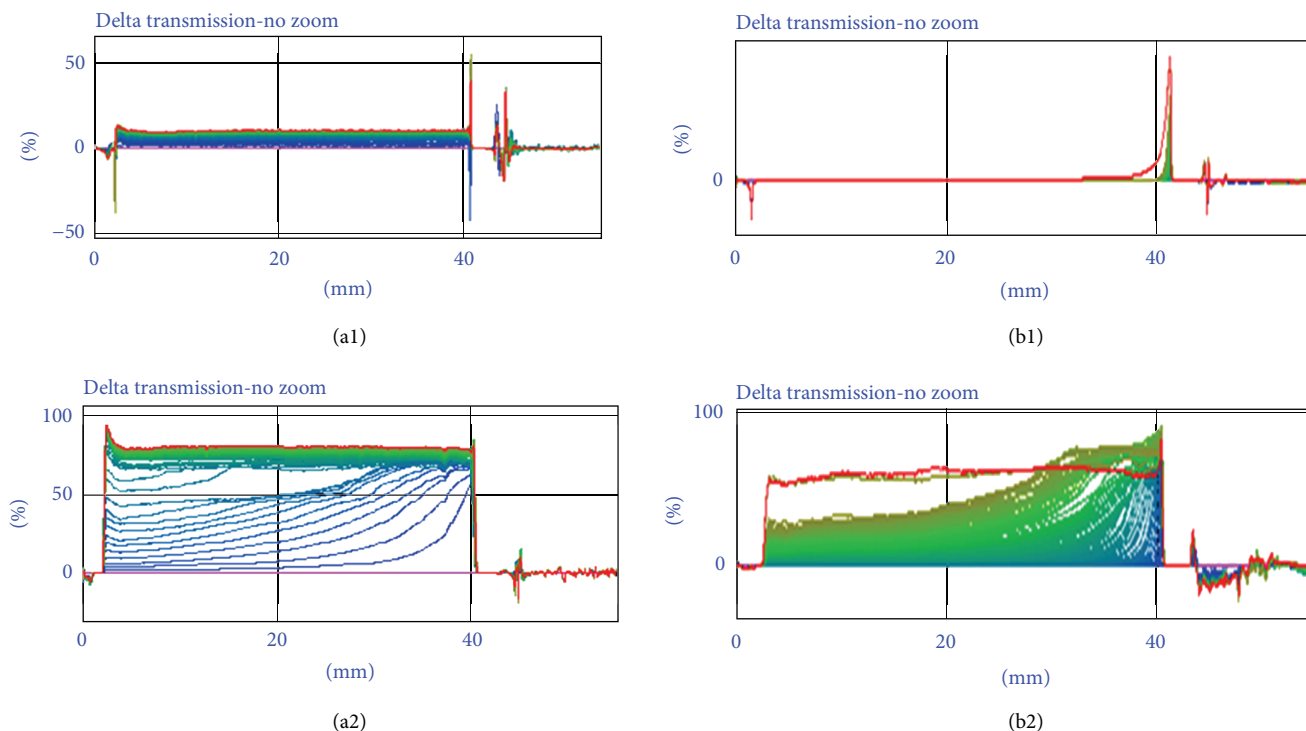


FIGURE 5: Transmission profiles for (a1) Ni@C and (a2) Ni nanopowders in ethanol and (b1) Ni@C and (b2) Ni nanoparticles in polyethylene glycol (PEG) at 25°C.

without a carbon shell. The dispersion stability kinetics of the PEG showed good dispersion. However, the sedimentation and flocculation behavior were observed in Ni nanoparticles without a carbon shell. The fully coated carbon shell layers of the Ni nanoparticles positively affected the stable dispersion in the fluid. Both the particle size and surface layer influence the magnetic hysteresis behavior of nanopowders.

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