PHYSICAL REVIEW B **71**, 024106 (2005)

Thermal history dependence of the crystal structure of Co fine particles

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(Received 10 May 2004; revised manuscript received 26 October 2004; published 19 January 2005)

hcp and fcc Co fine nanoparticles with different size have been synthesized by low-temperature laser pyrolysis and by reduction at different temperatures from 200 °C to 550 °C of cobalt-oxide nanoparticles prepared by the same method. The influence of thermal treatment on the crystal structure of Co particles was examined. It was found that below 420 °C, only hcp Co phase particles were obtained by laser pyrolysis or by reduction. Medium temperature (around 420 °C) resulted in a mixture of hcp and fcc phases. Only when high temperatures, above 500 °C, were involved during the synthesis or annealing of Co particles, did the fcc particles form and maintain their structure to ambient temperature, without structural change of fcc-hcp. In view of the size effect on the phase transformation kinetics, the stabilization of fcc Co particles was explained.

DOI: 10.1103/PhysRevB.71.024106 PACS number(s): 61.46.+w, 81.30.Kf, 78.67.Bf, 42.62.−b

I. INTRODUCTION

Fine magnetic particles have been attracting much attention because of their versatile applications and unique properties different from those of bulk materials.[1,2] It has been recognized that the magnetic properties of metallic particles are highly dependent on their crystal structure, size, shape, and composition. Accordingly, preparation of magnetic particles with different sizes and controllable crystal structures, as well as understanding the size dependence of crystal structure, are of technological importance to their application and development of novel magnetic materials.[2–4]

As a promising candidate for magnetic self-assembled structures (superlattices) that has potential application in ultracompact information storage, Co nanosized particles have attracted much interest in preparation and in structural and magnetism characterizations in the last several years.[4,5] As is well known, bulk cobalt is allotropic, exhibiting face-centered cubic (fcc) and hexagonal close-packed (hcp) structures above or below 420 °C, respectively.[6] Up to now, Co particles with different structures and sizes have been prepared by way of physical approaches (gas evaporation, sputtering, etc.) and solution-phase chemical routes.

However, the structure dependence of Co nanoparticles on the specific synthetic approach has not been well understood, and the explanations about the size dependence of the small Co particles remain controversial. For example, by solution chemistry (polyol or decomposition of carbonyl), fcc, hcp, as well as complex cubic ($\varepsilon-$) Co particles have been synthesized, depending on the additive nucleating agents, surfactants, and coordinating ligands.[4,7–9] Upon physical routes, including vacuum evaporation,[10–12] sputtering,[5,13,14] and plasma (or arc) discharge,[15–18] metastable fcc Co nanosized particles were preferentially produced at ambient temperature, although occasionally a mixture of fcc and hcp phases was formed.[19] Some authors attributed the existence or the stabilization of metastable fcc phase at low temperature to rapid cooling during the growth of the particles.[11] Actually, fcc-hcp structural change did not take place during a slow cooling from high temperature.[13] Recently, Kitakami *et al.*[20] proposed a size dependence of the crystal structure of Co nanoparticles on the basis of a consideration of contribution from surface energy. According to their analysis of energy change with the particle size, below a critical size (20 nm mean diameter) the stabilization of the fcc structure could be intrinsic stable; whereas hcp phase could be stabilized for particles with diameter above 40 nm. This proposal is not compatible with the fact that fcc Co particles with wide size distribution (up to 200 nm) can exist at room temperature.

In attempt to clarify the intrinsic nature of the stabilization of fcc Co particles, Co fine particles with different structures and different sizes were prepared at different temperatures. Much attention has been paid to the influence of thermal treatment or the thermal history on the structure evolution of Co particles.

II. EXPERIMENTAL

Co fine particles were prepared by a CO_2 laser induced pyrolysis of $Co_2(CO)_8$ vapor produced by evaporation of solid $Co_2(CO)_8$ crystals (Fluka Chemie GmbH) at 44 °C. Figure 1 shows a schematic of the experimental apparatus for the laser-induced pyrolysis. During the preparation process, a nonreactive chamber wall, small reaction area, as well as steep temperature gradients enable the formation of very fine and uniform particles. With comparison to other physical deposition techniques, such as vacuum evaporation, sputtering, and discharge, the laser-induced gaseous pyrolysis approach has no substrate on which the particles formed (or deposited), resulting in homogeneous nucleation and growth of the initial nuclei. In the pyrolysis, ethylene was used as photosensitizer to absorb CO_2 laser emission of P(20) line (wavelength 10.6 μm) and then to transfer the energy from the laser beam to the $Co_2(CO)_8$. In this procedure, a mixture of $Co_2(CO)_8$ vapor and C_2H_4 passed through a stainless steel nozzle (2 nm diam) and intersected vertically with a horizontal CO_2 laser beam (SYNRAD Duo-Lase model 57-2-150 W) with a spot 4 mm in diam. $Co_2(CO)_8$ vapor decomposed

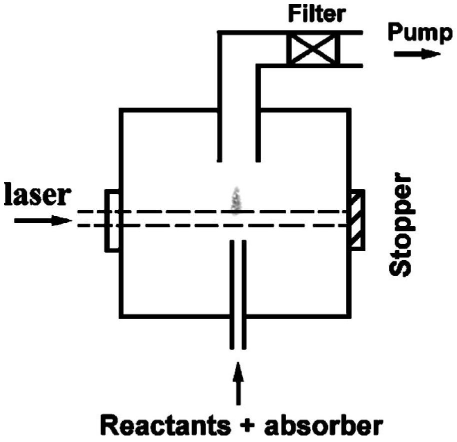

FIG. 1. Schematic representation of laser-induced pyrolysis.

in the reaction area and Co atoms nucleated homogeneously to form nanometer-sized particles. The laser-induced pyrolysis employed in the present work has been reported in detail elsewhere.[21] In the present study, unfocused laser beam with low power intensity was selected to obtain a low-temperature reaction area and to avoid dissociation of C_2H_4. Five K-type thermocouples were employed to determine the temperature distribution within the reaction area, and the highest temperature of reaction area was estimated by extrapolation of the measured temperatures.

Co nanoparticles and fine particles were also obtained by reduction of CoO particles under a H_2 flow at temperatures from 200 °C to 550 °C. A similar laser pyrolysis route was applied to synthesize CoO nanoparticles with $Co(CO)_3NO$ (Fluka Chemie GmbH) as precursor in a reduced atmosphere ($Ar+20\%H_2$) at laser power of 41 W, corresponding to a laser power density 326.4 W/cm^2. In order to avoid spontaneous combustion of as-prepared Co particles due to their active metallic nature, the particles were passivated in a mixture flow of $N_2+0.01\%O_2$ for 24 h before exposure to air. After the thermal treatment, a deep cooling of fcc particles was carried out by immerging the particles into liquid nitrogen (77 K) to observe if structural transition takes place.

The carbon content of the cobalt and the cobalt oxide samples prepared by laser-induced pyrolysis was determined by a carbon/sulfur determinator (CS-244). The morphologies and sizes of the Co particles were investigated by a transmission electron microscope (JEOL-2000EX-II). The structural evolution was analyzed by x-ray diffraction (XRD) with a PW1710 diffractometer (Philips, Cu Kα radiation).

III. RESULTS AND DISCUSSION

A. hcp Co nanoparticles by low-temperature laser pyrolysis

In order to avoid a contamination of samples resulting from the decomposition of the photosensitizer, unfocused laser beam with low power density was employed. In the present study, two power densities, 19 W and 44 W, corresponding to the average power density of 151.3 W/cm^2 and 350.3 W/cm^2, respectively, were selected to induce the pyrolysis of cobalt carbonyl vapor. The resulting temperatures of the reaction area were measured to be 325 °C and 427 °C, respectively. C/S determination indicated a presence of a few carbon in the two samples, 0.08 wt % and 0.12 wt %, respectively. Nevertheless, the appearance of a trace of carbon in the Co nanoparticles could not be attributable to the decomposition of the photosensitizer, C_2H_4. Actually, in our previous preparation of iron and iron nitride nanoparticles by laser induced pyrolysis of iron pentacarbonyl, a little amount of carbon (0.3–0.8 wt % for example) was always detected in the samples, irrespective of C_2H_4 or NH_3 as photosensitizer during the pyrolysis.[22,23] The formation of a few carbon in the laser-induced pyrolysis reaction might be related to a decomposition of CO at high temperature with the metallic particles as catalyst.[22] Because of much lower laser power density employed in the present experiment than that in the preparation of iron and iron nitride nanoparticles ($<2040\ W/cm^2$), as well as the lower activity of cobalt than iron to carbon, a much lower carbon content was derived during the preparation of Co nanoparticles.

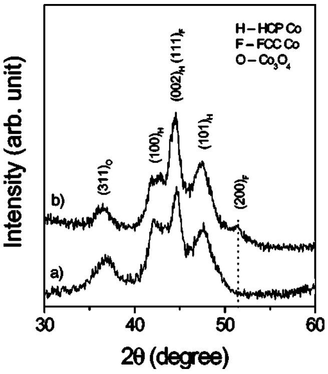

FIG. 2. X-ray diffraction patterns of Co nanoparticles prepared by laser pyrolysis: (a) at 325 °C and (b) at 427 °C, respectively.

Figure 2 shows the x-ray diffraction profiles of the particles prepared at these temperatures. It is noticed that both samples consist of metallic Co and cobalt oxide, Co_3O_4. It seems that the oxide is formed during the passivation process because there was no oxygen in the chamber during the preparation of the samples. Actually, it was experimentally demonstrated that the Co particles are spontaneously burned up if the powder was not subjected to a passivation procedure. Broad diffraction peaks are attributable to the small crystallite size of Co as well as Co_3O_4 phases. Referring to Seherrer formula, the average diameter of the Co crystals for both samples was estimated to be ~5 nm. It is worth noting that this value corresponds to the diameter of the Co core, not including the thickness of the oxide layer. Because of very small particle size, the amount of Co oxide takes a notable proportion in volume (or mass) of the samples, resulting in broad and evident peaks assigned to Co_3O_4 phase in the x-ray diffraction patterns, as shown in Fig. 2.

Figure 3 shows an electron micrograph of hcp Co nanoparticles prepared at 325 °C. The particles exhibit very fine and very uniform particle size, with an average diameter of 8.8 nm, including the core and oxide layer on the particle surface. The Co oxide layers formed on Co particles are uniform, with an approximate thickness of 1.5 nm. This value agrees well with the results of x-ray diffraction, sug-

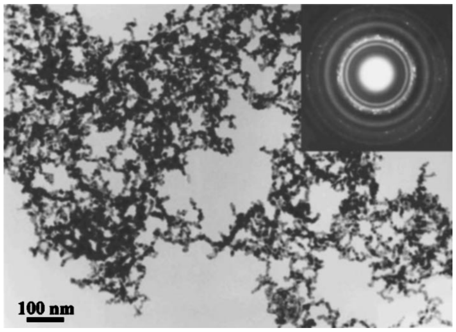

FIG. 3. Electron micrograph and corresponding selected area diffraction patterns of the hcp Co nanoparticles prepared at 325 °C.

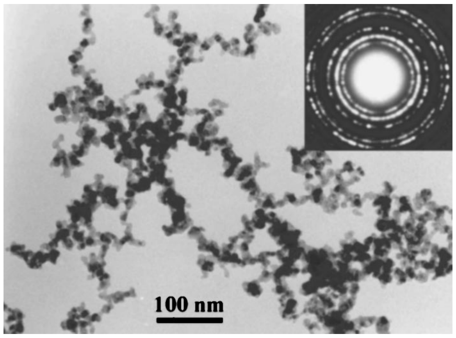

FIG. 4. Electron micrograph and corresponding selected area diffraction patterns of the CoO nanoparticles by laser pyrolysis.

gesting that most of the Co particles are single crystallites. Because of the same experimental parameters with exception of laser powers, the Co samples prepared at both temperatures are similar in particle size and morphology. As a matter of fact, during the preparation of nanoparticles by laser-induced pyrolysis, the particle size and morphologies are mainly related to the concentration of $Co_2(CO)_8$ vapor in the reaction area, especially when the temperature of reaction area does not vary greatly.

Although the Bragg angles (2θ) corresponding to the strongest diffraction lines for hcp and for fcc are different, which is, 44.77° and 44.22° for (002) and (111), respectively, it is very difficult to separate fcc and hcp phases because of the broadness of diffraction lines due to very small size of Co particles. Nevertheless, one can evidently confirm the existence of fcc phase upon diffraction peak due to (200) planes. Figure 2 illustrates clearly that the sample produced at lower temperature (325 °C) is comprised of hexagonal Co phase only. When the temperature of reaction area increases to 427 °C, cubic Co phase can be observed in the XRD patterns, suggesting that in this case the resulting sample is a mixture of majority of hcp phase and minority of fcc phase. Obviously, during formation of Co nanoparticles, temperature plays a key role in the achievement of their crystal structures. Further, even with the size regime of several nanometers, hcp is still the stable phase, rather than a metastable one.

B. hcp and fcc Co particles obtained by reduction of oxide nanoparticles

Figure 4 shows the TEM photograph of CoO nanoparticles produced by laser-induced pyrolysis of $Co(CO)_3NO$. The CoO particles are spherical in shape and exhibit a uniform size distribution with an average size of 11 nm diam. It is found that the CoO nanoparticles are not stable at high temperature. After a 200 °C oxidation in air for 30 min, CoO nanoparticles were further oxidized to Co_3O_4 without remarkable enlargement of particle size and without notable particle coalescence. A carbon analysis by C/S determinator demonstrated that no evident carbon was detected in the cobalt oxide samples to the limitation of analytical precision. Figure 5 represents the x-ray diffraction profiles of CoO nanoparticles prepared by laser pyrolysis and Co_3O_4 nanoparticles obtained by further oxidation at 200 °C. Both CoO and Co_3O_4 present a fcc crystal structure, with lattice constants of 0.426 nm and 0.809 nm, respectively. Taking these CoO and Co_3O_4 nanoparticles as precursors, reductions were performed at precisely controlled temperature from 200 °C to 550 °C in H_2 flow for 2 h. It is found that after reduction at low temperature far from the critical temperature at which mutual hcp-fcc transitions take place (such as 200 °C or 300 °C), both cobalt oxide particles, CoO or Co_3O_4, were converted to hcp Co particles. Figure 6 shows the electron micrographs and the corresponding diffraction patterns of the hcp Co particles obtained by reduction at 200 °C and 300 °C, respectively, in which no trace of fcc phase was detected. This is in good agreement with the x-ray diffraction measurements, as seen in Fig. 7. As the temperature of reduction increases from 200 °C to 300 °C, the average size of the hcp particles increases from 34 nm to 85 nm. It is suggested that during the reduction, a marked enlargement of particle size occurred by aggregation of small particles. Especially in the sample obtained by 300 °C reduction, some coalescence of hcp particles can be seen. In addition, the particles exhibit a wider size distribution than ones derived by 200 °C reduction, with the largest particles of 220 nm in size. When increasing the reduction temperature to 420 °C, fcc phase appears and then the Co particles were a mixture of fcc and hcp phases. With further increase of temperature up to 550 °C, single fcc phase was obtained, as shown in Fig. 7. During such high-temperature

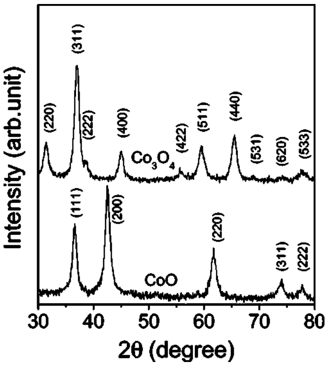

FIG. 5. X-ray diffraction patterns of CoO nanoparticles by laser pyrolysis and Co_3O_4 nanoparticles by reduction of the CoO precursor.

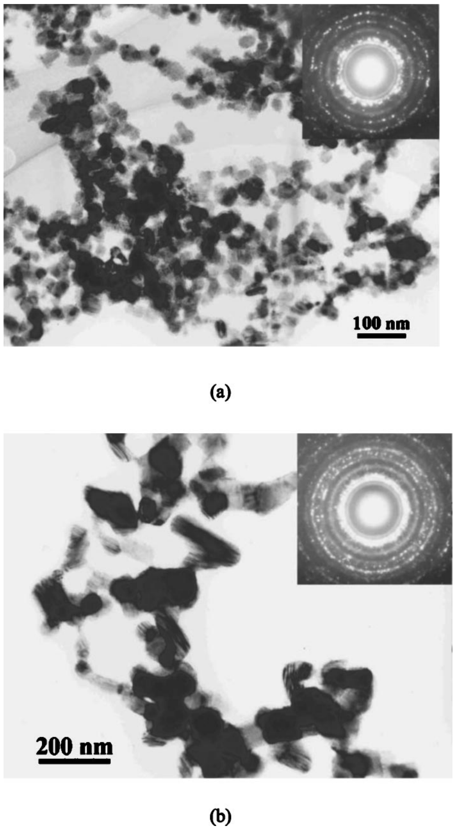

FIG. 6. Electron micrograph and corresponding selected area diffraction patterns of hcp Co nanoparticles prepared by the reduction of CoO nanoparticles at (a) 200 °C and (b) 300 °C.

reduction, the oxide nanoparticles and/or derived metallic Co particles undergo a remarkable growth by coalescence of small particles, leading to large Co particle in size (greater than 400 nm). After cooled to room temperature, the resultant metallic particles (with thin oxide layer on them) were immerged into liquid nitrogen (77 K) to examine whether structural changes take place or not. It is interesting to find by XRD diffraction that the Co particles remain fcc phase, no trace of fcc-hcp transition was observed. Consequently, in the range of particle size and temperature involved in the present experiments, the crystal structure of Co particles is only dependent on their thermal experience during the reduction, but independent on the particle size.

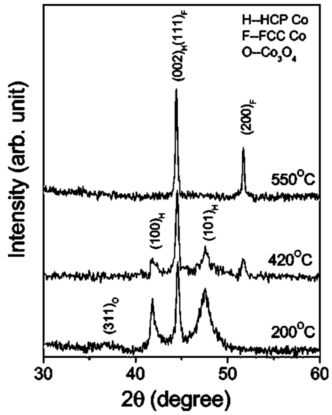

FIG. 7. X-ray diffraction patterns of Co particles prepared by the reduction of CoO nanoparticles at 200 °C, 420 °C, and 550 °C, respectively.

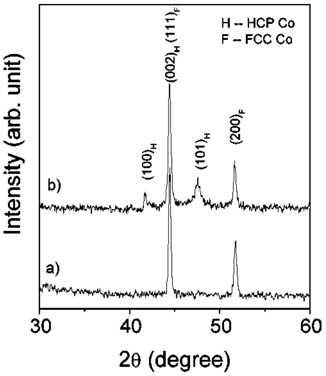

FIG. 8. X-ray diffraction profiles of the Co particles after a 3 *h* and 550 °C annealing of hcp nanoparticles by laser pyrolysis at 350 °C, (a) without and (b) with a gentle grinding during the XRD specimen preparation.

In order to confirm the stabilization of fcc Co particles with large particle size against fcc-hcp structural transition during the cooling from high temperature, as-prepared hcp nanoparticles were annealed at 550 °C in H_2 atmosphere for 3 h. As expected, after cooling to room temperature, fcc particles were obtained and no fcc-hcp transition was observed. However, we noticed that the fcc particles quite easily transform into hcp when a shearing stress is applied to them, even a mild grinding in the preparation of XRD specimen could cause a remarkable fcc-hcp phase transformation, as shown in Fig. 8.

C. Discussion

Bulk cobalt materials have been known to have two crystal structures, a fcc phase, which is thermodynamically preferred above 420 °C, and a hcp phase, which is favored at lower temperatures. However, a lot of experimental evidences suggest that upon physical deposition techniques, fcc Co fine particles with broad size range (from several nanometers up to 200 nm) were always obtained preferentially at room temperature. Obviously, size dependence of crystal structure proposed by Kitakami *et al.*[13,20] cannot give satisfactory explanation to these experiment data.

It should be noted that the preparation of Co fine particles by such mentioned physical approaches involves a nucleation and growth of Co at high temperature, or the particles formed by deposition of Co atoms with large kinetic energy, which is equivalent to high temperature. For example, the Co atoms produced by thermal evaporation in vacuum have the thermal energy nearly equivalent to its boiling temperature (2900 °C). Also, during the sputtering process, the kinetic energy of the Co atoms is estimated to have energy in the eV order, corresponding to very high temperature.[24] It is likely that the fcc Co particles form at high temperature and then keep their structure to ambient temperature under subsequent cooling or quenching. Experiment difficulties to achieve low temperature by physical techniques are probably the reason why fcc instead of hcp fine particles were frequently produced by vacuum evaporation (condensation) or by sputtering or other similar techniques.

In the present study, Co particles ranging from several nanometers to several hundred nanometers in size have been prepared by laser pyrolysis and by reduction of oxide at different temperatures. From our results, it is evident that the crystal structures of Co particles are closely related to their thermal history during the formation of the particles, and independent to their particle size in rather wide size range. Because of the vapor phase characteristics of laser pyrolysis of $Co_2(CO)_8$, the cobalt atoms nucleate homogeneously in the reaction area, resulting in Co nanoparticles with very small and uniform particle size. Only hcp nanoparticles were formed at 325 °C, which is far below the critical temperature of fcc-hcp or hcp-fcc phase transformations. This indicates that hcp Co is still the stable phase, when nanocrystals (or particles) are synthesized at low temperature, even for the particles with very small size. This result is in good accordance with the experiments of reduction of cobalt oxide nanoparticles at different temperature. In spite of the structural similarity between the fcc oxide (CoO and Co_3O_4) and fcc Co, hcp particles still formed after low temperature reduction at 200 °C and 300 °C. Only when high temperature is involved in the preparation or in the annealing process of Co particles, fcc particles with broad size range could be derived at room temperature. In other words, the fcc particles formed at high temperature and then kept their crystal structure to ambient temperature, exhibiting a different behavior from its bulk counterpart.

As is well known, fcc-hcp conversion of Co is achieved by martensitic transformation with a shearlike and displacive mechanism. In order for martensitic transformation to occur, a driving force (driving energy) is required to overcome the transformational resistance, i.e., the interfacial energy, and the strain energy resulting from the accommodation to shape changes of transformation. The driving energy can be supplied by lowering temperature (chemical-free energy) or by applying external forces (mechanical energy). It is reasonable to believe the stabilization of fcc Co particles to be related to a suppression of martensitic transformation during the cooling (or quenching) from high temperature to low temperature. In the light of phase-transformation kinetics, we attempt to develop an explanation for the stabilization of Co particles against fcc-hcp transition.

It has been argued that small particles are subjected to an extra pressure $\Delta P = 2\sigma_s/r$ because of surface tension, where σ_s is the surface tension and r is the radius of spherical particle. For bulk materials or large particles in the micrometer regime, the value of ΔP is very small and the influence on transformation behavior could be ignored. However, the extra pressure for very small particles would have prominent influence on the properties of the particles. For example, owing to surface tension, very small particles are in such a compression state that the lattice spacing decreases as the particle size decreases.[25–27] In this context, it is reasonable to believe that the extra pressure would exert an appreciable influence on the transformation behavior of small particles. This is because martensitic transformation occurs by shear mechanism, and, accordingly, the transformation would take place only when the driving energy resulting from the chemical Gibbs free-energy difference or from the external force exceeds the critical shearing energy barrier for phase transformation. Of course, this influence is associated with the physical properties of the metals or alloys in consideration, particularly, the critical driving force needed to trigger the transformation in bulk materials.

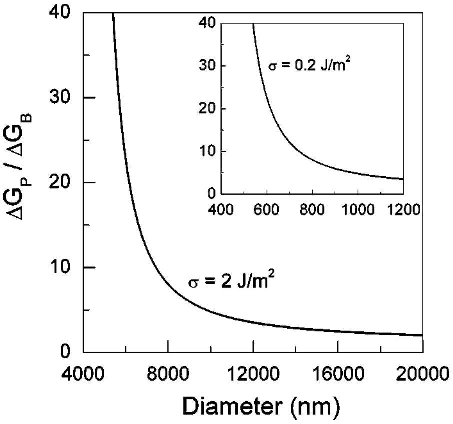

FIG. 9. The calculated generalized activation energy for martensitic transformation as a function of the diameter of Co particles at the surface energy of 2 J/m^2 and 0.2 J/m^2.

When considering the contribution of extra pressure, the critical activation energy for martensitic nucleation in parent phase can be expressed as follows:[28,29]

$$\Delta G = \frac{K}{(\Delta g + \Delta P)^4}, \tag{1}$$

where Δg is the critical driving force for martensitic transformation, K is a constant related to the elastic energy and interfacial energy between martensite and parent phases. Since Δg is negative and ΔP is positive, ΔG will increase with the increase of ΔP, i.e., decreasing in particle size. fcc-hcp transformation of Co involves the transition from one closed-packed phase to another, with a very small driving energy (−16 J/mol).[28] In this situation, even moderate or minor extra pressure (ΔP) could play an important role in impeding martensitic transformation of Co fine particles. This might be the reason why the fcc Co particles with rather wide size range could maintain their structure under cooling to ambient temperature. As a matter of fact, according to Eq. (1), a generalized critical activation energy ($\Delta G_P/\Delta G_B$) could be achieved if spherical shape and the surface energy of Co particles are assumed, where ΔG_B and ΔG_P are, respectively, the activation energies for bulk cobalt and for cobalt particles. With reference to the surface energy data of bulk cobalt (around 2.0 J/m^2)[30] and the critical driving force (−16 J/mol), the relationship between ΔG and the particle size is given in Fig. 8. In order to address the dependence of generalized activation energy on the surface energy, a plot with surface energy of 0.2 J/m^2 is attached on Fig. 9. It is indicated that only for Co particles several micrometers in size, the effect of surface energy on the transformation could be ignored; that is, fcc particles with rather broad size range could keep their structure during cooling from high temperature. This is in agreement with the present experiment results of acquirement of fcc particles with high-temperature reduction and annealing. Also because of small driving force, even a mild external force can overcome the critical driving force to induce fcc-hcp transformation of Co particles. Similarly, iron is allotropic and exhibits fcc-bcc structural change by martensitic mechanism. By contrast with cobalt, its transformation takes place with large driving force (approx $-1000\ \mathrm{J/mol}$[28]) and at very high temperature ($\sim 770\ ^\circ\mathrm{C}$). Consequently, metastable small fcc particles were hardly obtained at low temperature by physical deposition or by way of cooling from high temperature, unless additive elements, Ni or N for example,[17,29,31] were incorporated (alloying) to decrease remarkably the transformation temperature or deformation was applied to induce martensitic transformation.[16,29]

Regarding the different structures of Co nanoparticles synthesized by solution-phase chemical routes, small driving energy of fcc-hcp transformation is probably also an important factor. In this case, the influence of nucleating agents, surfactants, and coordinating ligands on the structural evolution of the particles in solutions would be dominant. Therefore, Co particles with hcp, fcc, even complex cubic (ε-Co) structures formed depend on the specific components of the solutions. The fact that ε-Co can be prepared only by solution chemistry demonstrates the strong effect of solution components on the development of different structures of Co particles. The nucleation and structural evolution of Co particle in chemical solutions is a complex process and detailed analysis and discussion is beyond the scope of the present study.

IV. CONCLUSIONS

Upon laser-induced pyrolysis and reduction of cobalt oxide nanoparticles at different temperatures, Co fine nanoparticles with different size and different crystal structures (hcp and fcc) have been synthesized. The crystal structures of Co particles depend on the thermal history involved during particle formation. Low-temperature pyrolysis or reduction of cobalt oxide favored the formation of hcp Co particles; metastable fcc phase can be achieved if high temperature was involved during the synthesis or annealing of Co particles. The stabilization of fine fcc particles is related to the suppression of fcc-hcp martensitic transformation, and fcc particles formed at high temperature retain their structure to ambient temperature.

ACKNOWLEDGMENTS

Thanks are due to the support from the Spanish Ministry of Education and Culture (No. SB2000-0289) for Foreign Professors, Researchers and Technologists. Financial support from the Natural Science Foundation of China under Project No. 50471002 is acknowledged.

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