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# Characterization of ultrafine Fe-Co particles and Fe-Co(C) nanocapsules

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Fe-Co ultrafine particles and Fe-Co(C) nanocapsules are characterized systematically regarding the phase structures, hyperfine fields, and magnetic properties. [S0163-1829(99)11129-9]

Ultrafine particles (UFP's) with a particle size below 100 nm have received much interest in the last two decades.[1–3] UFP's have been produced using several different methods, such as colloidal precipitation,[4] mechanical attrition,[5] and vapor deposition.[6,7] Multilayered carbon cages coating $LaC_2$,[8] $YC_2$,[9] transition metals, and nanocrystallites of transition-metal carbides[10,11] were discovered in carbonaceous deposits formed by electric arc discharge. From their size (below 100 nm) and protective nature, the carbon cages can be called ''nanocapsules.'' Nanocapsules are industrially important matter used as catalysts, magnetic materials, and so on.

Investigations have been done for UFP's of magnetic materials such as Fe,[12–14] Co,[15] Ni,[16] and their alloys.[17] Gangopadhyay[13] discovered a core-shell type of structure with an $\alpha$-Fe core and a coating of oxides (about 10–20 Å in thickness). The oxide layer is not continuous, but consists of very fine grains. It is a great interesting to study the structure and magnetic properties of Fe-Co(C) nanocapsules, since carbon may play an important role in the formation, structure, and magnetic properties of nanocapsules. However, to the best of our knowledge, few works have explored this topic. In this report, Fe-Co UFP's and their carbon-containing counterparts, namely, Fe-Co(C) nanocapsules, are prepared by evaporating the master materials of Fe-Co alloys in two kinds of atmospheres, i.e., a mixture gas of hydrogen and argon or a methane ($CH_4$) gas. The phase structure, hyperfine fields, and magnetic properties of the UFP's are systematically studied.

By electric arc discharge method, as used in our previous work,[18] bulk Fe-Co alloys to be evaporated served as the anode, while a carbon rod served as the cathode. After the chamber was evacuated, methane or a mixture of hydrogen and argon was introduced to reach $1.3\times10^4$ Pa as a reactant gas and a source of hydrogen plasma. The species of the layers covering on the surface of particles were determined by using x-ray photoelectron spectroscopy (XPS) measurements. Mössbauer spectroscopy was used to study the difference between hyperfine fields in bulk materials and their corresponding UFP's. Effects of carbon atoms on the phase structures and magnetic states in the Fe-Co(C) nanocapsules were investigated by means of x-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetization measurement. The composition in the fine particles was determined by means of energy disperse spectroscopy (EDS) and chemical analysis. Magnetization was measured by a vibrating sample magnetometer (VSM) at room temperature in a field up to 0.8 T.

For convenience, hereinafter the samples are referred to as (a)–(f), Fe-Co UFP's which were prepared in $H_2+Ar$ atmosphere and (A)–(F), Fe-Co(C) nanocapsules which were prepared in $CH_4$ atmosphere. The results of the composition analysis show that the content of carbon that came from $CH_4$ atmosphere increases with increasing Fe concentration in the samples of (A)–(F). This indicates that the iron allows combinations with carbon to form carbides or solid solutions as well as the carbon shell of nanocapsules. This result is in accordance with that of Fe-Ni(C) nanocapsules[19] in which the carbon content also increases with increasing Fe concentration. In the bulk iron-cobalt alloys, solid solutions form in a continuous range of composition, all of which are ferromagnetic.[20] Apart from the composition near 45 wt. % Co where only one bcc phase forms, two phases of fcc and bcc coexist in all composition range in the bulk Fe-Co system. Figures 1 and 2 represent XRD patterns of the Fe-Co UFP's and Fe-Co(C) nanocapsules, respectively. In contrast to the bulk Fe-Co system, the Fe-Co UFP's have a different phase constitution. Namely, two phases of fcc and bcc coexist below 40 wt. % Co, a bcc single phase exists near about 45 wt. % Co, the two phases coexist again above about 50 wt. % Co and a single fcc phase in pure Co particles. Fe-Co(C) nanocapsules have a similar phase constitution to that of the corresponding Fe-Co UFP's. In addition, the broaden of peaks in the XRD patterns bears evidence of that the mean size of each kind of UFP's is in the range of nanometers. The

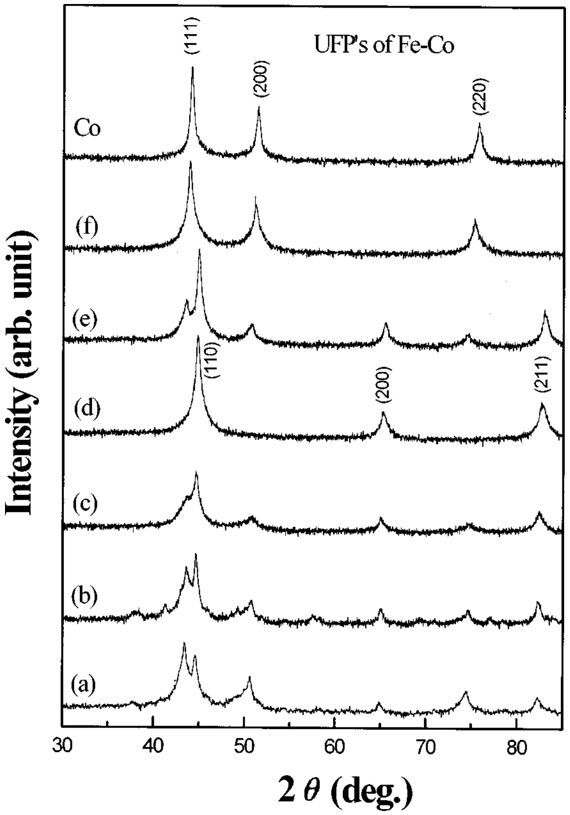

FIG. 1. X-ray diffraction patterns for Fe-Co UFP's [samples (a)–(f)] and Co particles.

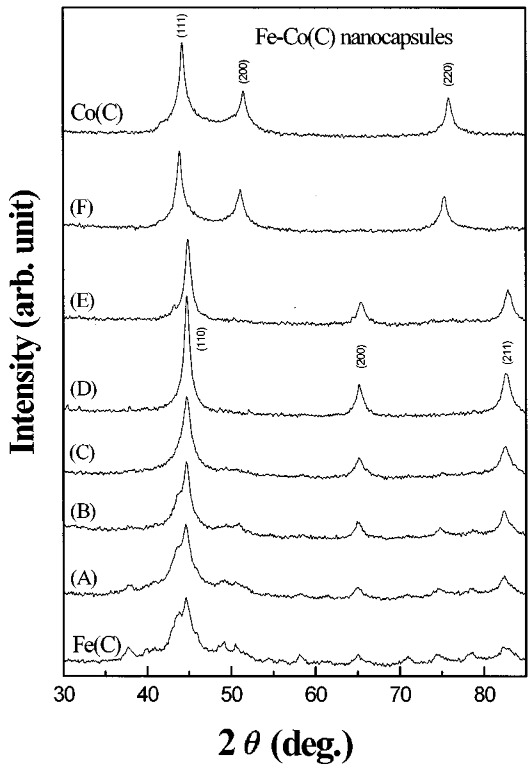

FIG. 2. X-ray diffraction patterns for Fe-Co(C) [samples (A)–(F)], Fe(C), and Co(C) nanocapsules.

mean size of the Fe-Co(C) nanocapsules (~10 nm) is smaller than that of the Fe-Co UFP's (~20 nm), consistent with the result of TEM micrographs.

Binding energies of Fe$2p_{3/2}$ electrons in compacted samples and surface cleaned samples were measured by analyzing XPS spectra as shown in Fig. 3. The typical samples of (d) and (D), corresponding to the Fe-Co UFP's and the Fe-Co(C) nanocapsules, respectively, were used for XPS measurements. It is shown that iron oxide (no cobalt oxide can be identified by XPS of Co$2p_{3/2}$ electrons) and pure Fe exist in the Fe-Co UFP's. After the surface of the UFP's was cleaned by argon ions sputtering, the amount of the iron oxide decreases. Since the surface of the UFP's cannot be composed of pure Fe atoms due to high surface energy, the peaks corresponding to the binding energies of pure Fe are ascribed to the core of Fe-Co solution particles. Only the Fe peak (no obvious peak for iron oxides) exists in the Fe-Co(C) nanocapsules, suggesting that a carbon layer on the Fe-Co(C) nanocapsules protects them from oxidization. According to the above results and our previous work,[18,19,21–23] it can be reasonably concluded that the Fe-Co UFP's form a core/shell structure with iron oxide layers and a Fe-Co solution core, and that the Fe-Co(C) particles are really nanocapsules with carbon cages and a Fe-Co(C) solution core.

The hyperfine fields increase initially with increasing cobalt content and reach a maximum near about 30 at. % Co, and then decrease with addition of more cobalt. Mössbauer effect at room temperature for fine iron particles[14] (16.4 and 40.4 nm) indicates that no observable peak for iron oxides and superparamagnetism emerges, except the pure iron six-line spectrum. The reasons for the absence of the iron oxides and the superparamagnetism in Mössbauer spectra are as follows. First, the Debye temperature for fine crystals of the iron oxides coating on the core of the UFP's is lower than room temperature. Second, the blocking temperature is shifted towards a higher temperature due to the magnetic interaction between the particles. The Mössbauer spectra at room temperature for the Fe-Co UFP's indicate that a transition from paramagnetism to ferromagnetism occurs near about 20 wt. % Co in the Fe-Co UFP's. The existence of the paramagnetism in the range of high Fe content is very interesting, which is not the case for the bulk alloys.[24] However,

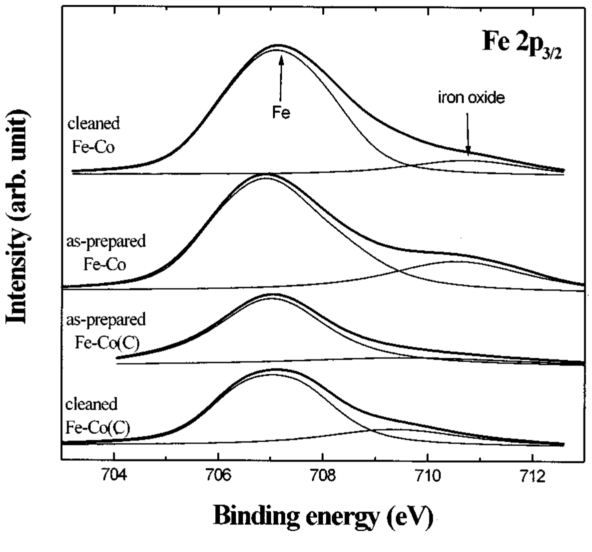

FIG. 3. Fe$2p_{3/2}$ x-ray photoelectron spectra of as-prepared Fe-Co, Fe-Co(C) particles and their surface cleaned samples.

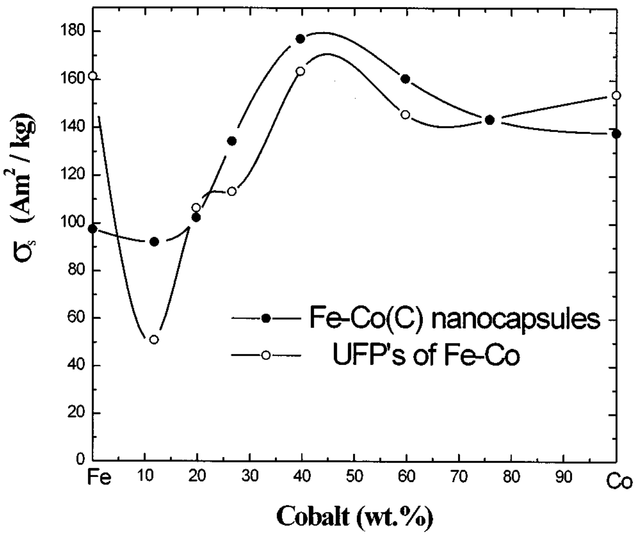

FIG. 4. Composition dependence of saturation magnetization in Fe-Co UFP's and Fe-Co(C) nanocapsules.

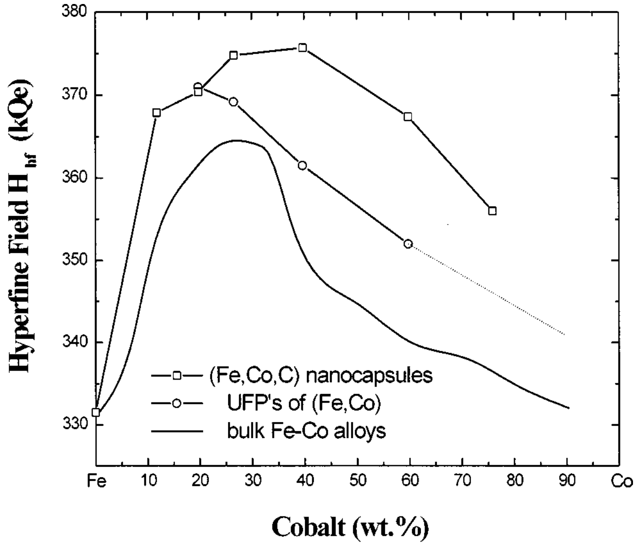

FIG. 5. Variation of the hyperfine fields at the $^{57}$Fe nucleus in Fe-Co UFP's and Fe-Co(C) nanocapsules. The curve for bulk Fe-Co alloys is presented for comparison.

the hyperfine fields in ferromagnetic phases of the Fe-Co UFP's decrease with increasing Co content, which have a similar composition dependence to that of the bulk Fe-Co alloys. In comparison to those of the Fe-Co UFP's, the constituent phases and the magnetic states are very complicated for the Fe-Co(C) nanocapsules. Effects of carbon atoms on the structure and magnetic properties are very obvious. The fitted parameters for Mössbauer spectra of the Fe-Co(C) nanocapsules[25] show that (Fe,Co,C) and (Fe,C) solutions as well as cementite $Fe_3C$ exist in all the Fe-Co(C) nanocapsules samples, and paramagnetic fcc-(Fe,C) disappears above approximately 40 wt. % Co.

The addition of cobalt in iron results in increasing saturation magnetization $M_s$ up to approximately 24.6 kG at about 36 wt. % Co in the bulk Fe-Co alloys.[24] Composition dependences of the saturation magnetization for the Fe-Co UFP's and Fe-Co(C) nanocapsules are given in Fig. 4 for comparison. It is seen that there is a similar tendency on the composition dependence of the saturation magnetization for the Fe-Co and Fe-Co(C) particles. The maximum of the saturation magnetization (at 36 wt. % Co) in the bulk Fe-Co alloys is shifted to be at 45 wt. % Co in the UFP's. Meanwhile, a minimum appears at about 10 wt. % Co in the UFP's systems. The saturation magnetization of the carbon-containing Fe-Co(C) nanocapsules is higher than that of the corresponding carbon-free Fe-Co UFP's.

Ar and C atoms (the latter comes from decomposition of $CH_4$) in the two kinds of atmospheres for evaporation have different contribution to the effect of condensation. It is known that carbon atoms have a slighter weight than argon atoms. Therefore, carbons are more beneficial to exchange their energies with the metal atoms through impact, affecting the kinetic process of constructing atomic clusters and subsequent UFP's. Such better effect for condensation causes smaller particles' size for the Fe-Co(C) nanocapsules, in comparison with that for the Fe-Co UFP's. This has been verified by the results of TEM (Ref. 25) and the broaden peaks in the XRD patterns. Bulk Fe-Co alloy with higher Fe content has relatively lower Curie temperature $T_c$ since Curie temperature $T_c$ of pure iron is lower than that of pure cobalt. Rapid quenching retains the paramagnetism of magnetic alloys at high temperatures to room temperature. During evaporating bulk Fe-Co alloys, the alloys with high iron content are easier to exhibit the paramagnetism in the form of UFP's. Comparing Ar and C atoms, the better effect of carbon atoms on condensation leads to that the paramagnetism occurs in a wider composition range for the Fe-Co(C) nanocapsules (above 50 wt. % Fe) than that for the Fe-Co UFP's (above 75 wt. % Fe). Besides the better effect of condensation, carbon atoms can also play a role as a reactant element to form (Fe,Co,C), (Fe,C) solid solution, $Fe_3C$ and carbon cage in the Fe-Co(C) nanocapsules. Although no carbon was detected by XRD, it could be concluded that a carbon layer forms on the surface of the Fe-Co(C) nanocapsules. It is reasonable that the great amount of interfaces existing in the UFP's may allow covering of the carbon layers of little thickness so that the content of carbon reaches as high as up to around 12–26 wt. % in the Fe-Co(C) nanocapsules.

As shown in Fig. 5, the hyperfine fields $H_{hf}$ in the Fe-Co UFP's and the Fe-Co(C) nanocapsules are increased in comparison with those of the corresponding bulk Fe-Co alloys. The composition dependences of the hyperfine fields are almost the same among the bulk and the particles. However, the hyperfine fields $H_{hf}$ of the Fe-Co(C) nanocapsules have the largest values. It is thought that carbon atoms affect the electron density near iron nucleus and increase the hyperfine fields. This is in good agreement with our previous work on Fe-Ni(C) nanocapsules.[19] The electron density in the Fe-Co UFP's decreases below about 30 wt. % Co and increases above 30 wt. % Co. It is concluded that carbon atoms increase the electron density and the hyperfine fields in the Fe-Co(C) nanocapsules, in comparison with the carbon free Fe-Co UFP's and the bulk Fe-Co alloys.

In conclusion, compared with bulk Fe-Co alloys, the Fe-Co UFP's and the Fe-Co(C) nanocapsules have a wide composition range for the coexistence of the two phases with bcc and fcc structures. A single bcc phase can be formed near about 40 wt. % Co in both kinds of the UFP's, which has the largest saturation magnetization. Carbon atoms which were dissolved from methane can be used to form a new core/shell type structure with a carbon layer and a core of (Fe,Co,C), (Fe,C) solutions, as well as $Fe_3C$ in the Fe-Co(C) nanocapsules. The hyperfine fields at the $^{57}$Fe nucleus in all the UFP's are increased in comparison with those of the bulk alloys. Carbon atoms which solidified in the (Fe,Co,C) solution exhibit a significant effect on the hyperfine fields by changing the electron density. The occurrence of the paramagnetism in the range of high iron content is attributed to the quenching caused by the impact between gas and metal atoms. Carbon atom has a better effect of condensation than argon atom, causing the existence of the paramagnetism in a wider composition range. The carbon layers on the surface of the nanocapsules have an excellent effect to resist them from oxidization.

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