High-coercivity Fe nanoparticles produced by coimplantation of Fe and C in Cu

G L Zhang and Shi-jun Yu

Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

Abstract. A novel method was developed to prepare iron nanocrystallite by using coimplantation of Fe and C in copper and subsequent heat treatment. The formation process of iron carbide and iron granules was monitored by means of conversion-electron Mössbauer spectroscopy, and the particle size was determined by transmission electron microscopy. Cementite, Fe_3C, was formed after annealing at 300 °C, then transformed to α-Fe particles with a size of about 25 nm. Magnetic coercivities of 1.15 kOe and 0.37 kOe for the Fe granules have been observed at room temperature (RT) and 80 K, respectively. A retained carbon-enhanced effect was proposed to explain the strong coercivity at RT.

1. Introduction

Magnetic nanocrystallites are of great interest because of their unusual properties, with diverse potential technical applications [1]. Many methods have been developed to obtain these nanosized particles [2, 3]. Significantly high coercivities for Fe particles were found. The highest values, of 1.05 kOe and 1.1 kOe at room temperature, respectively, for sizes of 14 and 20 nm, were obtained by vapour deposition [4, 5].

Studies have shown that the coercivity of the particles is strongly influenced by the interaction between the Fe oxide shell and the Fe core [4]. Recently we developed a new method for producing Fe particles in SiO_2 and Cu using ion implantation [6, 7]. It is well known that the Fe is thought to be insoluble in these substrates. Fe ions, however, can be embedded in SiO_2 and Cu by implantation with energetic ions. A subsequent annealing process then leads to iron atoms precipitating from these matrices. The sizes of the particles can be controlled by the implanted-ion energy and dose. In this paper, we study the influence of carbon atoms on the coercivity of the Fe grains by using coimplantation of Fe and C ions in the Cu substrate. The results showed that the coercivity for the iron granules was much enhanced by the presence of carbon atoms. The coercivity value obtained is even larger than the result of Gangopadhyay *et al* [4], but the influence of the surface layers of Fe oxide is excluded.

2. Experimental details

A copper polycrystallite was used as the substrate, with a thickness of 60 μm and a purity of 99.99%. The ^{57}Fe and ^{12}C ions were implanted successively in the substrate at RT. The energy for the ^{57}Fe ions was 80 keV, whereas for ^{12}C implantation an energy of 20 keV was

chosen to ensure a maximum overlap of the calculated ^{57}Fe and ^{12}C depth profiles. The mean projected range calculated by TRIM is about 22 nm. The doses were 5×10^{16} atoms cm^{-2} and 1×10^{17} atoms cm^{-2} for ^{57}Fe and ^{12}C, respectively. The beam currents implanted in an area with a diameter of 10 mm on the Cu were about 0.3 μA and 1 μA, respectively for ^{57}Fe and ^{12}C. After implantation the sample was annealed for 30 min in a hydrogen atmosphere at a pressure of 4×10^4 Pa from a temperature of 200 °C to 500 °C. Conversion-electron Mössbauer spectroscopy (CEMS) was performed to determine the location and state of the Fe ions for the as-implanted sample and their evolution after the subsequent annealing. A source of ^{57}Co in Pd and a resonant counter with 5% CH$_4$ in a He gas flow were used for the CEMS. The CEMS spectra were fitted using a least-squares fitting program with isomer shift (IS) values calculated with respect to α-Fe. The magnetic properties were measured by using a vibrating-sample magnetometer (VSM) with an external-field range from 0–16 kOe for room and liquid nitrogen temperatures, respectively. The size of the Fe grains was determined by transmission electron microscopy (TEM).
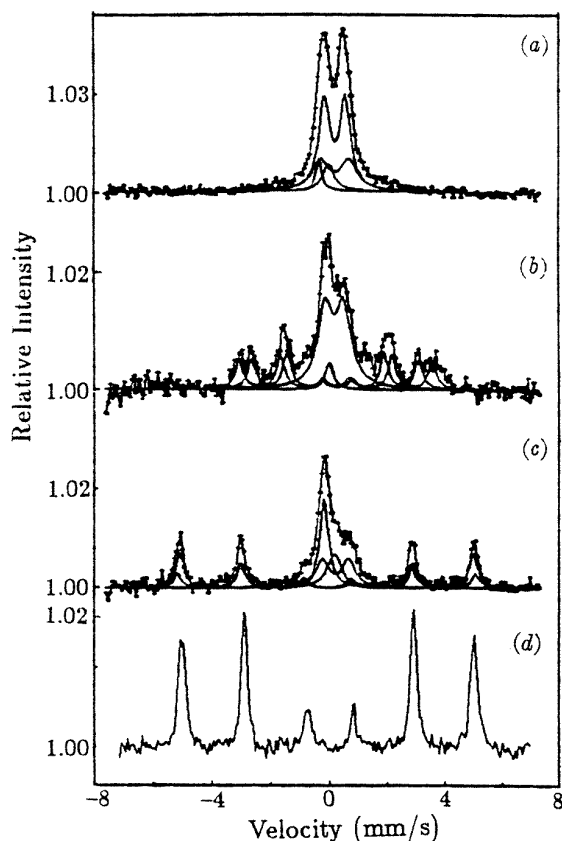

Figure 1. CEMS spectra for the sample obtained by coimplantation of ^{57}Fe and ^{12}C in Cu at RT as functions of the heat treatment: (*a*) RT; (*b*) 300 °C for 30 min; (*c*) 500 °C for 30 min; (*d*) α-Fe.

3. Results and discussion

Four typical CEMS spectra are shown in figure 1. The figure clearly shows an evolution of the Fe state and precipitate with annealing temperature. For the Fe/C-implanted sample the spectrum (figure 1(*a*)) is quite similar to the one with only implanted Fe. The spectrum can be resolved into four components corresponding to four different Fe sites. A new iron carbide component appeared in the spectrum in addition to isolated iron atoms, clusters with a doublet, and γ-Fe which were identified in the sample with as-implanted Fe in Cu [7]. The isomer shift and quadrupole splitting of the iron carbide are 0.22 mm s^{-1} and 0.78 mm s^{-1}, respectively. This might be attributed to a superparamagnetic ε-Fe$_2$C hexagonal carbide [8].
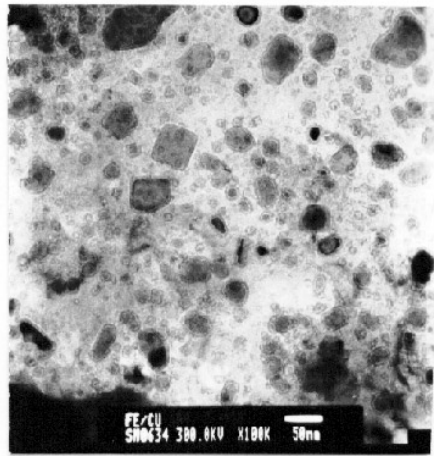

Figure 2. A TEM micrograph of a Cu sample obtained by coimplantation of ^{57}Fe and ^{12}C after annealing at 500 °C for 30 min.

After annealing, the relative intensities among the isolated iron atoms, clusters, γ-Fe, and iron carbide changed due to the migration of Fe, C atoms and vacancies. It was found that a significant change of the spectrum pattern had already taken place after the annealing at 200 °C. A component with a wide linewidth corresponding to a small hyperfine magnetic field occurred in the spectrum. This indicates that the isolated atoms started aggregating and the clusters growing. After the annealing at 300 °C, two sets of sextet patterns can be well resolved in the spectrum, as shown in figure 1(*b*). The values of their hyperfine (hf) fields are 19.0 T and 20.2 T, respectively. Upon annealing at 450 °C for 30 min, those hf fields changed to 33.0 T and 20.8 T, respectively, with corresponding isomer shifts of 0.01 mm s^{-1} and 0.19 mm s^{-1}. From those values the two components obviously can be attributed to α-Fe and Fe$_3$C (cementite), respectively. The intensity ratio of the α-Fe to Fe$_3$C is about 27%. Interestingly, all of the cementite transformed to α-Fe after the annealing at 500 °C. The sextet for this phase can be further decomposed into two components with slightly different hf fields and isomer shifts, as shown in figure 1(*c*). In terms of a consideration of the nanocrystalline structure, they are probably due to the crystalline and the surface atoms of the iron grains, respectively. The relative intensity of the α-Fe component in the spectrum is about 60%. A typical TEM micrograph is shown in figure 2, where the iron

grains whose presence was confirmed by electron diffraction patterns are clearly displayed. The average size estimated is about 25 nm.
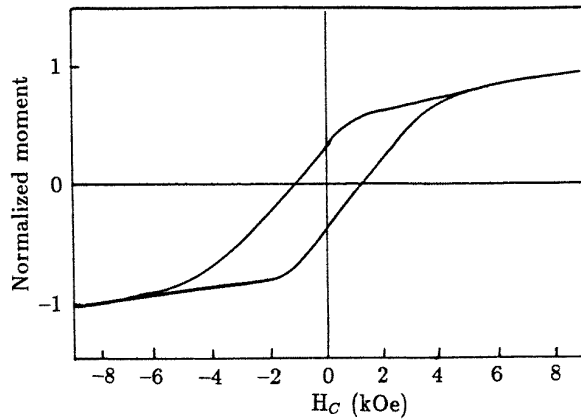

Figure 3. The magnetic hysteresis loop of the α-Fe sample, with conditions as for figure 2.

A magnetic hysteresis loop for the α-Fe granules in Cu measured at RT is shown in figure 3. The coercivity H_c obtained was 1.15 kOe at RT. The value is somewhat larger than the one obtained by coating the α-Fe particles with Fe oxide. In our case, surface oxidation was excluded. Therefore, so strong an H_c cannot be explained by the interaction between the Fe oxide shell and the Fe core [4]. The H_c-value is much larger than the one obtained by using a high rate of magnetron sputtering in the Fe–(SiO$_2$) system [3].

According to conventional theories [9], for single-domain Fe particles, the zero-temperature coercivity H_{c0} is $2K/I_s$, where I_s is the saturation magnetization and K is the effective anisotropy constant from various contributions—magnetocrystalline, shape, stress, etc [10]. It is well known that the vacancies and even cavities are produced by a cascade of atomic collisions during implantation. The Fe atoms have a very low solubility in Cu metal, and therefore strongly tend to precipitate within cavities above certain annealing temperatures. The iron-precipitate-driven growth of cavities would take place with a high stress associated with these growth processes. This phenomenon somewhat resembles that of inert gas precipitating as a crystalline solid under certain implantation conditions at RT [11, 12]. The α-Fe particle with the high stress probably brings about the high coercivity. Furthermore, these particles are quite well separated. Therefore, under such conditions the percolation effect [3], which leads to a decrease in H_c due to dipole interaction between particles, is negligible. In addition, an important reason for the high value of H_c is probably the C atoms which are retained in the interstitial sites of the α-Fe particles. It is well known that the value of H_c of bulk steel with carbon is much higher than that of purified iron, due to the C acting as a pinning site for domain wall motion. The interstitial C atoms might further increase the stresses in the crystal and enhance the anisotropy constant (K). This idea was proved using a sample with only Fe implanted in Cu, for which a value of H_c of 70 Oe was obtained at RT. Moreover the highly aspherical shape of the particles, as shown in figure 2, may have also brought about the increase of the effective anisotropy constant (or H_c).

Normally with an increase of temperature the value of H_c should decrease due to thermal agitation destabilizing the magnetic moments of the single-domain particles. The temperature dependence of H_c should obey the Kneller–Luborsky formula [13], $H_c = H_{c0}(1 - \sqrt{T/T_g})$, where T_g is the onset temperature for superparamagnetism. Thus as T decreases, H_c should increase. But the value of H_c obtained at 80 K for the coimplanted sample after annealing at 500 °C was 370 Oe, which is much smaller than that at RT. As is known, the critical radius R of a single magnetic domain is proportional to $\sqrt{K}/I_s$ [14], the value of which actually decreases with decrease of temperature. The sizes of the Fe particles shown in figure 2 are just around the critical value. Therefore the single domain might become a multidomain structure at 80 K, leading to a decrease of the coercivity H_c [6]. In addition, changes in local strain with temperature may also decrease the local anisotropy.

4. Conclusions

For a sample with iron and carbon coimplanted in copper, cementite Fe_3C was formed following annealing at 300 °C. This transformed to α-Fe grains of size about 25 nm after further annealing at 500 °C. For this system of granules in a Cu substrate, a coercivity of 1.15 kOe was obtained at room temperature. The high coercivity may result from interstitial C atoms, and local strain in the Fe crystal arising from the precipitation growth processes and from the highly aspherical shape of the particles. At 80 K a coercivity of 0.37 kOe was observed. We tentatively suggest that this may be due to the onset of incoherent reversal processes at lower temperatures.

Acknowledgments

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