Superparamagnetic Fe clusters in Ag matrix produced by sputter-gas aggregation

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Experiments to generate a thin composite Fe-Ag film employing a sputter-gas-aggregation process are described. The magnetic properties are studied at low temperatures. In addition, the morphology is determined by high-resolution transmission electron microscopy and the structure by using x-ray diffraction and XAFS. Small clusters of about 11 Å in diameter are highly dispersed in an Ag matrix. They show the characteristics of interacting superparamagnets. © *1995 American Institute of Physics.*

Over the past years increasing interest has been focused on nanoscale granular materials because they are considered as candidates for many potential technological applications[1] due to physical properties which deviate remarkably from the corresponding bulk properties.[2] The cluster size turns out to be one of the key parameters controlling these properties. Usual preparation techniques such as mechanical milling of fine powders and annealing of supersaturated solid solutions provide only crude control of this sensitive parameter. In contrast, the sputter-gas aggregation technique[3] allows rather precise control of the cluster size.[4] They are grown from supersaturated metal vapor, transferred by a liquid N_2-cooled Ar gas stream towards a substrate where they are softly deposited. Since Fe particles are known to exhibit superparamagnetic behavior in the nanometer size range,[5] Fe is used as a magnetic sensor to demonstrate the efficiency of the sputter-gas aggregation technique. The present letter describes a first successful experiment to generate Fe clusters up to sizes of about 100 Å which are highly dispersed in an Ag matrix.

A thin film of about 0.5 μm thickness with a Fe/Ag of 27/73 was prepared by 24 h codeposition at room temperature from independently sputtered Fe and Ag targets using the sputter-gas aggregation technique. The Ar gas pressure in the sputter chamber was kept at about 0.5 Torr.

The crystal structure of the resulting shiny metallic film was determined by employing conventional x-ray diffraction and Fe *K*-edge XAFS. A separate specimen prepared under similar sputter and condensation conditions was used for a TEM study of the nanoscale structure. The chemical fluctuation in the nanometer range of the film was investigated by an attached energy dispersive x-ray (EDX) analyzer. Temperature- and field-dependence of the magnetization were measured using a SQUID magnetometer.

The obtained granular Fe/Ag film exhibits a broad face-centered-cubic (fcc) Ag-like diffraction pattern as shown in Fig. 1. The shift of the Ag(111) peak to the high angle side is due to a shrinkage of the Ag lattice constant originating from the high amount of Fe dispersed in Ag. The Ag(111) peak broadening is assumed to be due to the granular character of the Ag matrix consisting of Ag particles. Their size is estimated from the halfwidth of the Ag(111) peak using the Scherrer equation to be of the order of 10 nm. Since the Bragg peaks of Fe and Ag are overlapping, XAFS was used to obtain further insight into the near neighbor structure of the Fe component. The correlation function deduced from XAFS (Fig. 2) reveals a strongly distorted Fe structure which deviates markedly from the bulk body-centered-cubic (bcc) one. The peak around 2.2 Å can be assigned to the Fe-Fe correlation, the peak at around 2.8 Å to the Fe-Ag correlation. The transmission electron microscopy (TEM) investigation reveals a similar feature. The high-resolution micrograph (Fig. 3) shows the granular structure of the film with a clear lattice appearance of the deposit, whereas Fe lattices cannot be identified. The most direct experimental signature of the granular character of the Fe/Ag film stems from an EDX investigation of the corresponding TEM sample which reveals chemical fluctuations of about 50% around the average composition on the nanometer scale.

Further support for the view that the granular metal film consists of ultrafine Fe-particles with rather uniform sizes and dispersion can be obtained from magnetic measurements.[6] The remanence, M_r, at a given temperature, T, is a measure of the volume fraction of single-domain particles which behave as ferromagnets against thermal agita-

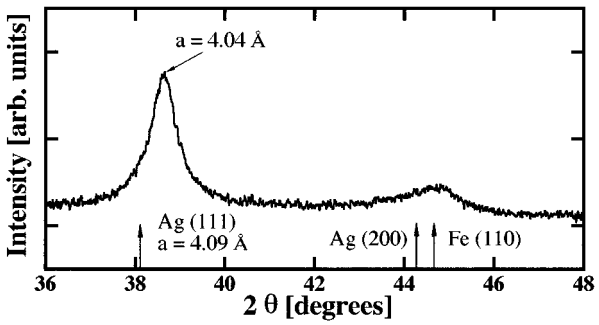

FIG. 1. Diffraction pattern of granular $Fe_{27}Ag_{73}$. The arrows indicate the Ag(111), (200), and the Fe(110) Bragg peaks of the respective bulk materials.

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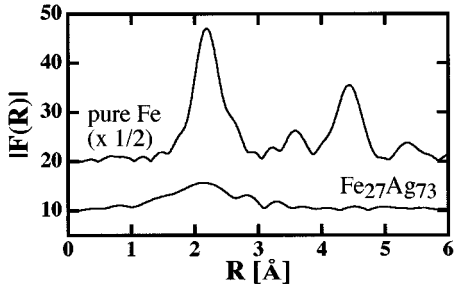

FIG. 2. The correlation function $|F(R)|$ of Fe as a function of the distance, R, in comparison with pure bcc Fe as obtained by XAFS. The intensity of the pure Fe was reduced by a factor of 2.

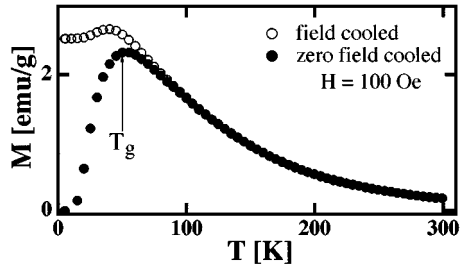

FIG. 4. The temperature dependent remanence, M_r and coercivity, H_c. The inset displays volume distribution, $\Phi(V)$, as a function of the particle diameter, D.

tion in the timescale of the measurement. Applying the method of Weil *et al.*[7] the cluster size distribution can be estimated from the temperature dependence of H_c and M_r[8] with an accuracy comparable with several other techniques. The decay of H_c and M_r as a function of T is displayed in Fig. 4. Assuming a linear behavior of the initial magnetization curve, the diameter, D, can be calculated using the following equation:

$$D=2\left(\frac{3kT}{(1-M/M_s)4\pi M_s H}\right)^{1/3},$$

where M is the magnetization and H the applied magnetic field. The saturation magnetization, M_s, is estimated by extrapolating M as a function of $1/H$ to infinite field to be about 150 emu/g_{Fe}. The deduced volume distribution $\Phi(V)$ as a function of D is shown in the form of a histogram in the inset of Fig. 4. It displays an extremely narrow size distribution around a maximum at about 11 Å. A long tail appears towards higher D values up to 120 Å. This size range and the distribution consistent with the structural characteristics observed by x-ray diffraction and XAFS.

The reduced magnetization, M_r/M_s in Fig. 4 approaches about 0.4 at 0 K, which is lower than the Stoner–Wohlfarth value of 0.5 for a randomly oriented spherical, single domain system.[9] This indicates a slightly preferred orientation of the cluster moments or a deviation from the spherical shape. H_c of about 800 Oe at 0 K is much larger than 50 Oe for the bulk Fe.[10] The latter is a strong indication that the small clusters are uniformly dispersed in the matrix.

Figure 5 shows the temperature dependence of the field-cooled and zero-field-cooled magnetizations at $H=100$ Oe. For $T>T_g$ the system shows superparamagnetic behavior, where T_g corresponds to the maximum in the temperature dependence of the zero-field-cooled magnetization. A maximum appears as well in the field-cooled magnetization curve which is shifted to slightly lower T. A superparamagnetic system containing noninteracting ferromagnetic single domain particles displays a single reduced magnetization, M/M_S vs H/T curve at temperatures $T>T_g$. Since the present system does not obey this relation, M/M_S is plotted as a function of $(H+\omega M)/T$ in Fig. 6. The term ωM with $\omega=150$ Oe^2 g^{-1} erg^{-1} represents an additional magnetic field which is induced by magnetic interparticle interactions which is generally assumed to be a linear function of M.[11,12] An excellent superposition for $T>100$ K of several magnetization curves is obtained whereas the curves for $T<100$ K deviate.

In conclusion, we have obtained ultrafine Fe clusters embedded in an Ag matrix by the sputter-gas aggregation technique. Structural and magnetic investigations reveal a very narrow cluster size distribution with a halfwidth of about 20 Å and a maximum around 11 Å. The single domain Fe particles are magnetically interacting in a superparamagnetic

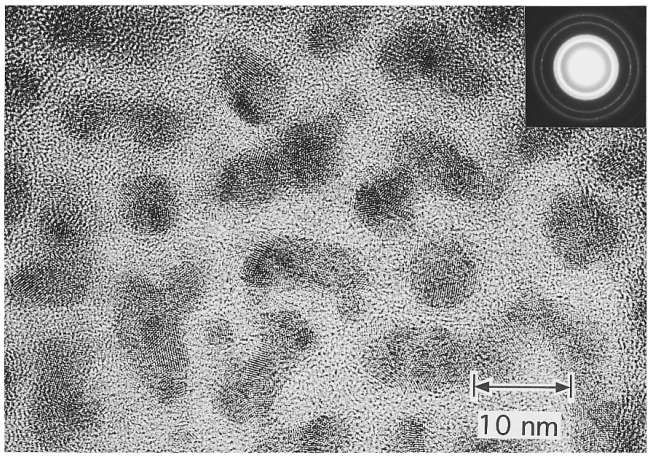

FIG. 3. TEM high-resolution micrograph of granular $Fe_{27}Ag_{73}$ with the corresponding diffraction pattern.

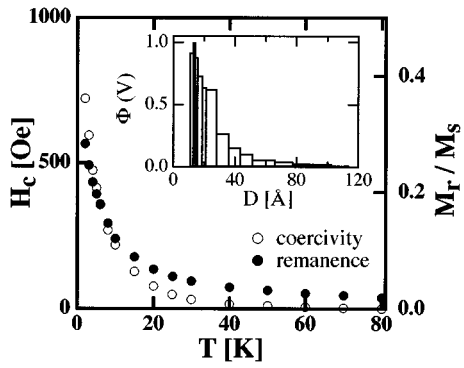

FIG. 5. Field-cooled and zero-field-cooled magnetization as a function of the temperature, T, in an applied field of $H=100$ Oe.

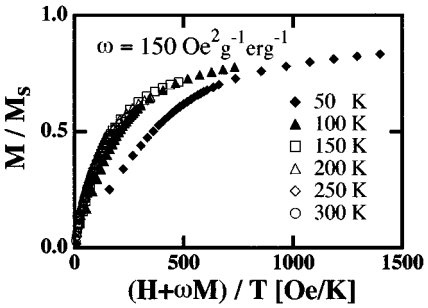

FIG. 6. Reduced magnetization, M/M_S, for several temperatures as a function of the temperature reduced total magnetic field $(H+\omega M)/T$.

phase above a transition temperature of about 100 K.

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