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The preparation and magnetic properties of Fe–Ag granular solid using a sol–gel method

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The Fe–Ag granular metal solid samples with 10% and 30% weight iron have been successfully fabricated using a sol–gel method, which are characterized by X-ray diffraction and transmission electron micrography. The average diameters of iron particles are from about a few nanometres to a few tens of nanometres controlled by the reducing temperature. The evolution of magnetic properties and microstructure during heat treating are described in detail and explained by using the superparamagnetism, single domain and multi domain theories. The magnetic anisotropy of the Fe–Ag granular solid is studied by using the law of approach to saturation. It is found that the magnetic anisotropy constant is in the order of 10^5 J m^{-3} which is higher than the value of the bulk iron and increases with the increase of reducing temperature.

1. Introduction

Granular iron solids have been paid more attention in recent years because of their interesting physical properties and their potential applications, for example in magnetic recording, optical devices and sensors [1, 2, 3]. In the past, granular iron solids with iron particles of size 2–20 nm have been prepared by codeposition of iron with an insulator such as SiO_2, BN, Al_2O_3 or metals such as Cu and Ag, which form matrices in which iron particles are embedded [3–6]. The magnetic properties of this kind of granular film have already been investigated. Recently, a sol–gel method was used to prepare nanosized iron particles surrounded by copper matrix (Fe–Cu granular solid) [7]. But the magnetic properties of this kind of material have been studied less and the magnetic anisotropy of this material is still unclear. In this paper, another metal matrix silver is tried and the Fe–Ag granular solid is prepared. The dependence of the magnetic properties and microstructure on the preparing condition is investigated and the magnetic anisotropy of this Fe–Ag granular solid is studied by using the law of approach to saturation.

2. Experimental methods

The sol–gel method has been already proved to be an effective way to prepare the nanocomposites [7–10]. In this work, a sol–gel method was used to prepare the Fe–Ag granular solid. The precursor compounds used for the present work were $Fe(NO_3)_3 \cdot 9H_2O$, and $AgNO_3 \cdot 3H_2O$, respectively. An aqueous solution of the compounds was prepared by dissolving the weighed amounts of these in 10 cm^3 distilled water. A few drops of concentrated nitric acid were added to the mixture to obtain a clear solution. The latter was stirred and heated at around 60 °C for 30 min. The solution gelled by drying it in an oven at atmosphere pressure at 100 °C ± 10 °C for a few hours. The dried gel was then ground into powders of about 0.1 mm diameter and then subjected to a reduction treatment in hydrogen from 350 to 500 °C.

The crystallographic structure of the samples was determined by X-ray diffractometry (XRD). The microstructure was studied using a transmission electron microscope (TEM). The magnetic properties of the samples were measured using a vibrating-sample-magnetometer (VSM) at room temperature with 2T maximum magnetic field.

3. Results and discussion

Fig. 1 shows the XRD patterns of Fe–Ag granular solid with 10 wt % iron reduced at different temperatures. It is shown that the iron in the Fe–Ag is b.c.c. structure and the silver is f.c.c. structure. It also can be found that there is a little Fe_3O_4 and Ag_2O. The effect of increasing the heat-treatment temperature is to increase the size of metal particles. It can be found from Fig. 1 that the sample reduced at 350 °C produced broad diffraction peaks and the sample reduced at 450 °C yielded much narrower peaks.

Fig. 2 is a typical electron micrograph for Fe–Ag granular solid with 10 wt % iron reduced at 400 °C for

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45 min. The particles are seen to be roughly spherical in shape. Selected areas of electron diffraction were also observed, and found to be in agreement with the XRD results. From the X-ray diffraction peak width (FWHM), a calculation of values of the average grain size were obtained using Scherrer's formula, $D = (0.9\lambda)/[\delta(2\theta)\cos\theta]$, where $\lambda = 0.154$ nm is the CuK_α wavelength, $\delta(2\theta)$ is the Fe(1 1 0) peak width corrected for instrumental broadening, and 2θ the scattering angle [11]. Table I gives the result of the iron average particles size for the Fe–Ag granular solid samples with 10 wt % iron reduced at different temperatures.

Fig. 3 shows a typical magnetization curve and a hysteresis curve at room temperature obtained for Fe–Ag granular solid sample with 10 wt % iron reduced at 400 °C for 45 min. The coercivity (H_c) is found to have a value of 19.89 kA m^{-1}, which is much higher than that of pure iron. It is evident, therefore, that the fine iron particles synthesized by the sol–gel method have a single-domain configuration.

The saturation magnetization for the Fe–Ag granular solid samples with 10 and 30% iron concentration versus the reducing temperature (T_c) for 45 min is shown in Fig. 4. The saturation magnetization increases with the increase of the reducing temperature for both 10 and 30 wt % iron Fe–Ag granular solid. The saturation magnetization of the iron particles in the 30 wt % iron Fe–Ag granular solid reduced at 475 °C reaches to 1.57×10^6 A m^{-1}, which is very near to the value for bulk iron which is 1.73×10^6 A m^{-1}. Here the original iron particle concentration 30 wt % in granular solid is used to calculate the iron saturation magnetization. In fact, the actual iron concentration in the granular solid is very near to the original one. The existence of a little iron oxide which can be found from the XRD results maybe causes this slight decrease of magnetization from 1.73×10^6 A m^{-1}. It is known that the average size of the iron particles increases with the increase of the reducing temperature and there

TABLE I The average size of the iron particles in the Fe–Ag granular solid reduced at different temperatures T_c

T_c (°C)	350	400	450	475
$\bar{D}$ (nm)	12.6	16.3	20.4	23.2

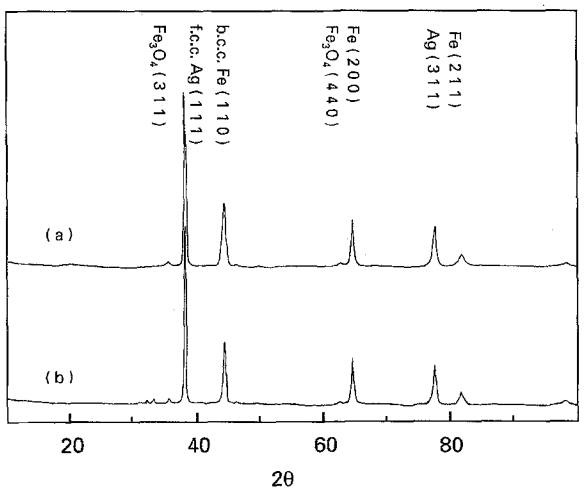

Figure 1 XRD patterns of a Fe–Ag granular solid with 10 wt % iron reduced at (a) 350 °C and (b) 450 °C for 45 min.

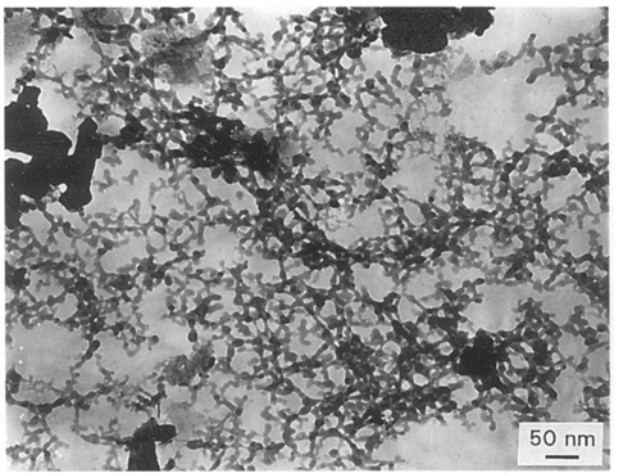

Figure 2 TEM micrograph of a Fe–Ag granular solid reduced at 400 °C for 45 min.

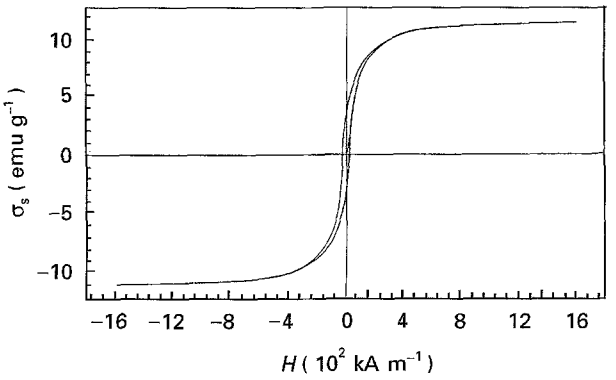

Figure 3 The magnetization curve and hysteresis curve at room temperature for a Fe–Ag granular solid reduced at 400 °C for 45 min. (1 emu g^{-1} = 10^3 ρ A m^{-1}, ρ is the density of the material in cgs units, 1 Oe = 79.58 A m^{-1})

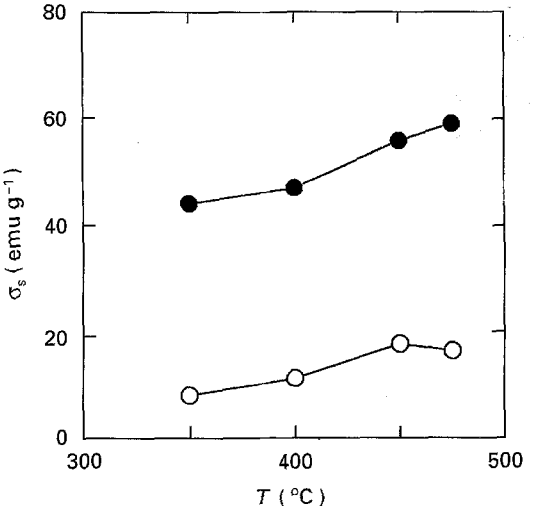

Figure 4 The dependence of the specific saturation magnetization on the reducing temperature for the Fe–Ag granular solid with 10 wt % iron (○) and 30 wt % iron (●).

is wide size distribution of the iron particles which can be found from the TEM micrographs of these granular solid samples. So, the proportion of the superparamagnetic particles for samples reduced at higher temperature is smaller than that for samples reduced at lower temperature. This causes the increase of the saturation magnetization of these Fe–Ag granular solid samples with the increase of the reducing temperature.

Fig. 5 shows that the coercivity varied with the reducing temperature for 45 min; it shows a maximum value at about $T_c = 400\,^{\circ}C$ for the 10 wt % iron Fe–Ag granular solid and a great decrease at $T > 400\,^{\circ}C$ for the 30 wt % iron Fe–Ag granular solid because the proportion of the thermal stable single domain particles is greatest for the Fe–Ag granular solid sample reduced at about $T_c = 400\,^{\circ}C$. It is well known that the critical size for the formation of a single magnetic domain in iron particles is in the order of a couple of tens of nanometres, but the precise value depends on the shape of a particle and its magnetic anisotropy [12]. This single-domain configuration causes ultrafine iron particles to exhibit much larger coercivities than that of bulk iron. The decrease of the coercivity for the 10 wt % iron Fe–Ag granular solid samples reduced at $T_c < 400\,^{\circ}C$ may be caused by the increase of the proportion of the superparamagnetic iron particles in the Fe–Ag granular solid which show superparamagnetic relaxation and have zero coercivity. The average size of the iron particles of the 30 wt % iron Fe–Ag granular solid is larger than that of the 10 wt % iron Fe–Ag granular solid reduced at the same temperature. So, the proportion of the single domain particles in the 30% iron Fe–Ag granular solid samples is more than in the 10% iron Fe–Ag granular solid samples reduced at lower temperature. This may be the reason for the (almost) invariation of the coercivity for the 30% iron Fe–Ag granular solid at $T \leq 400\,^{\circ}C$ (see Fig. 5). The decrease of the coercivity for the Fe–Ag granular solid samples reduced at $T_c > 400\,^{\circ}C$ may be caused by the increase of the proportion of the iron particles with multidomain which causes the soft magnetic properties with smaller coercivities.

The magnetization process for the Fe–Ag granular solid samples was measured. The value of the effective magnetic anisotropy constant is obtained from the magnetization data using the law of approach to saturation, which has already been proved to be an effective way for the granular solid materials [13–15]. The magnetization M_H changes with magnetic field H according to the equation when the magnetization approaches saturation

$$M_H = M_s\left(1 - \frac{a}{H} - \frac{b}{H^2} - \ldots\right) + \chi_p H \qquad (1)$$

and

$$b = \frac{1}{M_s^2}\left(\frac{8}{105}K_1^2 + \frac{4}{15}K_E^2\right)$$

$$K_E^2 = K_{sh}^2 + \frac{9}{4}\lambda^2\sigma^2$$

where K_1 is the magnetocrystalline anisotropy constant and the K_E the effective anisotropy constant including the contribution of the stress anisotropy and shape anisotropy. M_s is the saturation magnetization, and χ_p is the high-field susceptibility, λ is the magnetostriction constant and σ the stress. The effective magnetic anisotropy constant can be obtained from the above equations when the magnetization curve is measured. The detailed process for using the law of approach to saturation to calculate the effective anisotropy can be found in reference [15]. Fig. 6 shows the calculated effective magnetic anisotropy for the Fe–Ag granular solid samples versus the reducing temperature. It can be found that the value of the effective magnetic anisotropy constant is in the order of $10^5\ J\,m^{-3}$ which is higher than the magnetocrystalline anisotropy for the bulk iron and it is shown that the effective magnetic anisotropy constant increases a little with the increase of the reducing temperature.

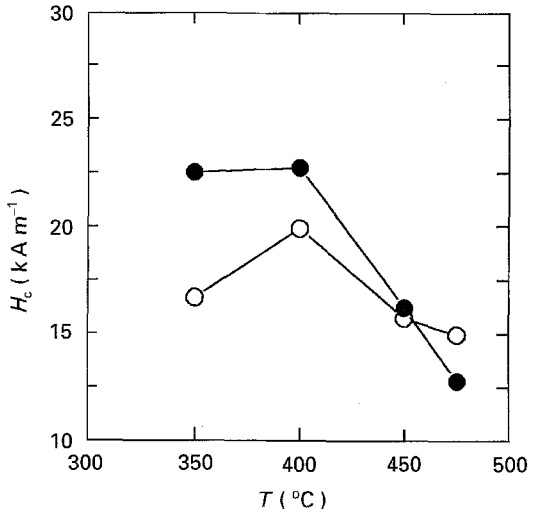

Figure 5 The dependence of the coercivity on the reducing temperature for the Fe–Ag granular solid with 10 wt % iron (○) and 30 wt % iron (●).

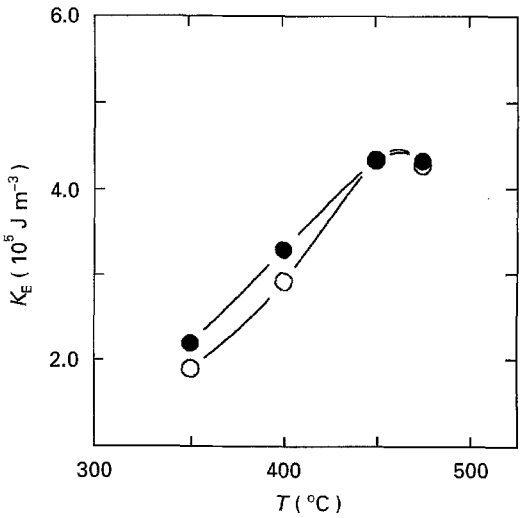

Figure 6 The dependence of the effective magnetic anisotropy constant on the reducing temperature for the Fe–Ag granular solid with 10 wt % iron (○) and 30 wt % iron (●).

The effective anisotropy includes the contribution from the stress anisotropy and shape anisotropy. The increase of the effective anisotropy with the reducing temperature may be caused by the increase of the stress with the increase of reducing temperature which causes the increasing of stress anisotropy.

4. Conclusions

In this work, the magnetic Fe–Ag granular solid samples are successfully fabricated by using a sol–gel method. The crystalline structure and microstructure of these materials are investigated by using XRD and TEM. The magnetic properties of these materials are studied, including the influence of the reducing temperature on the magnetic properties of the Fe–Ag granular solid samples. The effective magnetic anisotropy obtained by using the law of approach to saturation for the Fe–Ag granular solid samples versus reducing temperature are discussed.

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