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# Magnetic Properties of the Granular Alloy $Fe_{10}Ag_{90}$ as a Function of Annealing Temperature

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$Fe_{10}Ag_{90}$ granular alloys have been prepared using a sol-gel process, sintered at 300 °C and annealed at temperatures between 400 °C and 700 °C. The mean size of the iron particles, obtained from X-ray diffraction, is 30.0 ± 0.7 nm. Due to the existence of a distribution of particle sizes in these samples, both blocked (BL) and superparamagnetic (SPM) particles are present simultaneously, as confirmed by magnetization measurements at room temperature. AC susceptibility measurements as a function of temperature reveal a magnetic phase transition at about 770 °C, indicating the presence of particles exhibiting bulk behavior, in the samples annealed above 550 °C. The presence of these particles has been attributed to an atomic diffusion process between the grains, forming bulk-like multiple-domain Fe particles having Curie temperatures near that of bulk α-Fe phase ($T_C$ = 770 °C).

**Keywords:** *superparamagnetism, granular alloy, size distribution*

## 1. Introduction

The synthesis of nanometer-scale materials has been the focus of intense study in materials science and solid-state chemistry[1,2]. Nano-sized particles of noble metals have attracted considerable interest in various fields of chemistry and physics because of their conspicuous physiochemical catalytic properties and their potential applications in microelectronics, optical, electronic, and magnetic devices[3-6]. Much attention have been paid to granular iron solids because of their interesting physical properties, in particular, the discovery of giant magnetoresistance (GMR)[7,8] and giant magnetoimpedance (GMI)[9], as well as their application in magnetic recording and optical devices and in sensors[10-12].

Nanocrystalline Fe particles containing a single magnetic domain exhibit very different magnetic properties from those of bulk Fe. New applications require materials that combine high magnetization and coercivity of single domain Fe particles with a highly conducting matrix. Iron can form alloys or solid solutions with almost all metals, there being few metallic elements with which Fe is immiscible. Ag is an example of such a metal. However, in recent years, it has been shown that metastable and homogeneous alloys of Fe-Ag system can be formed by using special techniques, such as thermal evaporation[13,14], liquid quenching[15], ion implantation[16], sputtering[17-21], mechanical alloying[22-24], gas condensation[25] and a sol-gel process[26-28]. FeAg granular alloy, however, is metastable, and upon recrystallization at elevated temperatures, a transformation into separated phases of BCC Fe and FCC Ag occurs.

In this work a series of $Fe_{10}Ag_{90}$ granular alloys has been produced by a sol-gel method and characterized by X-ray diffraction and magnetization measurements. We have observed that in all samples there are particle size distributions composed of SPM and BL particles. A method for fitting the magnetization curve to a size distribution with these two components has been applied to determine their relative amounts[29]. The changes in annealing temperature $T_{ann}$ have a strong influence in the coercive field. The presence of particles exhibiting bulk behavior has been observed by AC susceptibility measurements in the samples annealed above 550 °C.

## 2. Experimental

$Fe_{10}Ag_{90}$ granular alloys were produced by a sol-gel process[26-28]. The start solution was prepared from an aqueous solution of Fe and Ag nitrates and nitric acid. The precursor powder obtained was reduced in a hydrogen atmosphere for 45 minutes at a temperature of 400 °C. The resultant powder was pressed and sintered at 300 °C for 8 hours. After sintering, the samples were thermally treated in the temperature range of 400-700 °C.

The crystalline structure of the samples was investigated by conventional X-ray powder diffraction using a Rigaku diffractometer operated with a Mo-$K_\alpha$ radiation tube.

The magnetization and hysteresis curves were measured in a vibrating sample magnetometer (VSM) with a maximum magnetic field of 1 T. AC susceptibility was measured in a mutual inductance bridge as described previously[30].

## 3. Results and Discussion

Figure 1 shows the X-ray patterns of powdered $Fe_{10}Ag_{90}$ granular alloy reduced at a temperature of 400 °C, sintered at 300 °C and annealed at $T_{ann}$ = 700 °C. It is seen that the iron in $Fe_{10}Ag_{90}$ has a b.c.c. structure and the silver has an f.c.c. structure; there are also some low

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intensity reflections from $Fe_3O_4$. Assuming that the Fe in the sample is indeed distributed as small particles, the average particle diameter should be related to the Fe Bragg peak widths by Scherrer's formula. Figure 2 shows part of the diffraction pattern shown in Figure 1 in the interval of 34.4-35.6 (2θ) for samples annealed at 400, 450, 500, 550, 600 and 700 °C. The Bragg peaks for Ag(222) and Fe(211) were fitted with a pseudo-Voigt function in order to determine the line width. Applying Scherrer's formula, we obtain the average Fe particle sizes $D_m$ from the (211) line width for different annealing temperatures, as shown in Table 1. $D_m$ increases from 28.6 nm (powder) to 30 nm (sintered sample). However, $D_m$ is only slightly affected by $T_{ann}$, staying at around 30 nm for all thermal treatment temperatures.

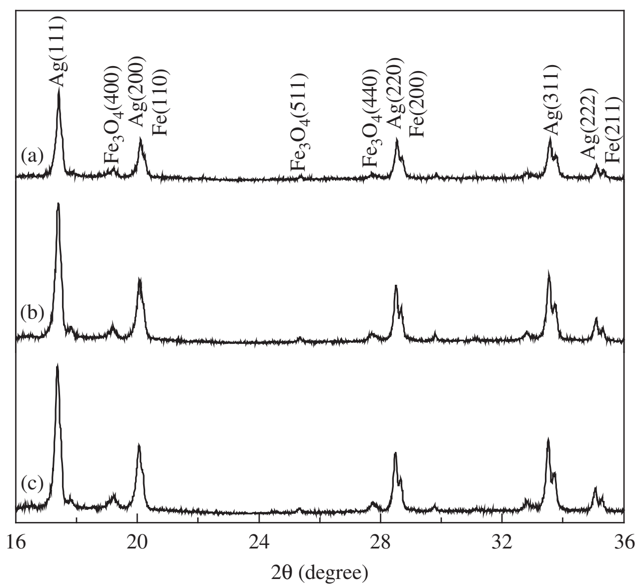


**Figure 1.** X-ray powder patterns of $Fe_{10}Ag_{90}$ granular alloy. a) Powder; b) Sintered at 300 °C; and c) Sintered at 300 °C and annealed at $T_{ann}$ = 700 °C.

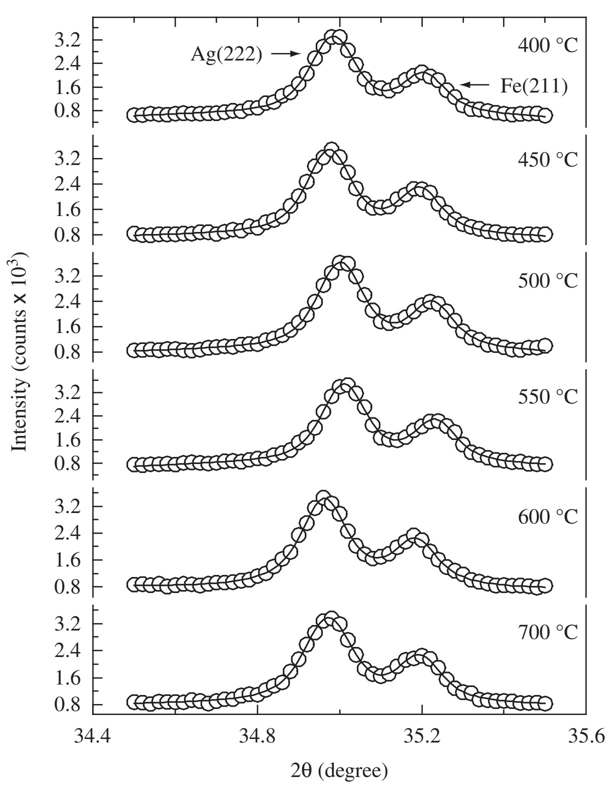


**Figure 2.** X-ray powder patterns of the Ag(222) and Fe(211) peaks of $Fe_{10}Ag_{90}$ granular alloy, at different annealing temperatures. The solid lines are the fittings obtained using two Pseudo-Voigt functions.

Figure 3 shows the hysteresis curves at room temperature obtained for $Fe_{10}Ag_{90}$ granular alloy samples annealed at different temperatures. The coercive field, determined from the hysteresis curves, ranges from 365 to 295 Oe, and is two orders of magnitude greater than that of bulk iron, showing the presence of blocked single-domain particles. These curves do not saturate in fields of up to 1 T, indicating the additional contribution of SPM particles. The figure insert shows the maximum field magnetization $M_{Hmax}$ as a function of the annealing temperature, and it can be seen that $M_{Hmax}$ decreases linearly with increasing $T_{ann}$, up to $T_{ann}$ = 500 °C. However, there is an inflexion at $T_{ann}$ = 550 °C, after which $M_{Hmax}$ once again decreases linearly with $T_{ann}$, but more rapidly. The inflexion at $T_{ann}$ = 550 °C suggests the formation of a different type of particle at this temperature. These particles appear to be larger than the blocked particles, and have multi-domain properties similar to bulk Fe. We attribute their presence to an atomic diffusion process between the grains. Above the inflexion, the proportion and size of large particles increases, and $M_{Hmax}$ therefore reduces quickly with $T_{ann}$. This explanation is supported by AC susceptibility measurements as a function of temperature, as shown in Figure 4. It can be seen that at $T_{ann}$ = 550 °C, there is a phase transition at 766 °C, near to the Curie temperature $T_C$ of pure bulk iron, $T_C$ = 770 °C. The transition temperature and the susceptibility drop at this temperature both increase with $T_{ann}$. This type of behavior has been observed in other systems[31].

Figure 5a shows the remanence $M_r$ as a function of annealing temperature. $M_r$ decreases with increasing $T_{ann}$, despite a small peak at

**Table 1.** Average Fe particle sizes $D_m$ in the $Fe_{10}Ag_{90}$ granular alloy at diferent $T_{ann}$ values.

| $T_{ann}$(°C) | 400 | 450 | 500 | 550 | 600 | 700 |
|---|---|---|---|---|---|---|
| $D_m$(nm) | 30.0 | 30.7 | 30.5 | 30.2 | 29.3 | 30.1 |

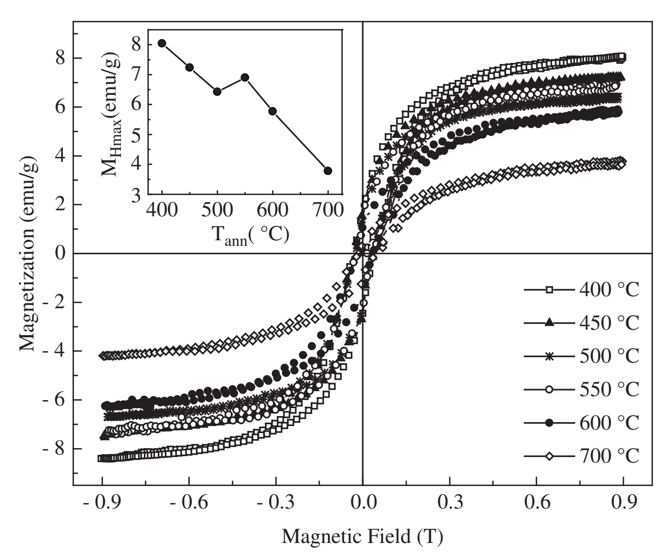


**Figure 3.** Room temperature hysteresis curves of the $Fe_{10}Ag_{90}$ granular alloy samples for different annealing temperature. Insert: maximum field magnetization as a function of $T_{ann}$.

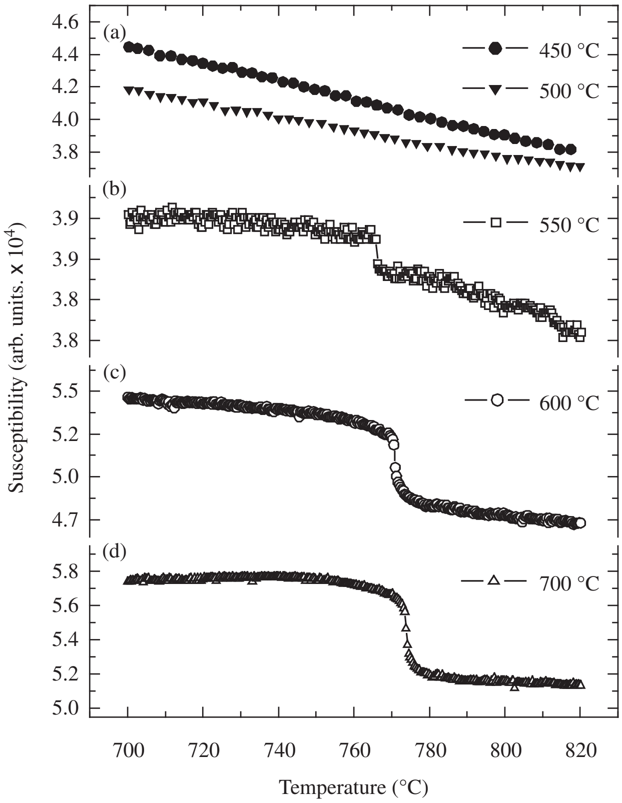


**Figure 4.** AC susceptibility of the $Fe_{10}Ag_{90}$ granular alloy samples at different $T_{ann}$: a) 450 and 500 °C; b) 550 °C; c) 600 °C; and d) 700 °C.

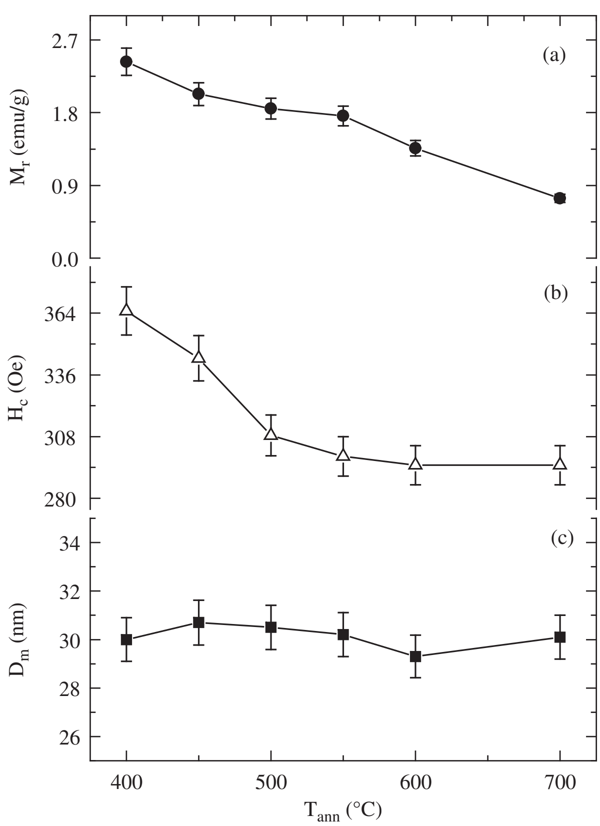


**Figure 5.** Magnetic properties of $Fe_{10}Ag_{90}$ prepared at different annealing temperature. a) Remanent magnetization; b) Coercive field; and c) Fe mean particle diameter obtained from X-ray diffraction.

550 °C, as seen in hysteresis curves. Figure 5b shows the coercive field $H_c$ *vs.* $T_{ann}$. One can see that $H_c$ decreases signicantly with increasing of $T_{ann}$, reaching a steady value of 295 Oe at $T_{ann}$ = 600 °C. This saturation in coercivity is probably due to the fact that for $T_{ann}$ = 600 °C there is a large number of bulk-like particles, as observed through the AC susceptibility curves (seen Figure 4). Another important observation may be made by comparing the coercive field with the average Fe grain size, displayed in Figure 5c, as a function of $T_{ann}$. We see that while $H_c$ change significantly with $T_{ann}$, $D_m$ stays almost constant at around 30 ± 0.7 nm. Thus, there is not a correlation between $H_c$ and $D_m$, as there is in a non-interage uniform particle system. However, in these samples there is a distribution of particle size. Both BL and SPM particles are present simultaneously, as confirmed by Mössbauer effect and magnetization measurements at room temperature[28], even though the critical diameter of Fe spherical particle is 16 nm[32], i.e. much less than $D_m$. Thus, heat treatment mainly modifies the distribution of particle sizes, and consequently the coercive field, which is a sum of contributions of all Fe particles in samples.

## 4. Conclusions

Samples of $Fe_{10}Ag_{90}$ granular alloys were thermally treated at various temperatures. Magnetic measurements show the existence of a distribution of particle sizes in these samples, which are composed of both SPM and BL particles. The magnetic properties of the samples are strongly influenced by changes in annealing temperature. For the samples annealed above of 550 °C appears a multidomain phase similar the $\alpha$-Fe phase, that was attributed to a process of atomic diffusion between the grains of Fe.

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