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We demonstrate a novel method for enhancing the coercivity of magnetic materials. Granular Fe-(SiO_2) solids have been fabricated over a wide volume fraction range from 15% to 100%. Giant magnetic coercivity, as high as 2500 Oe, has been observed in granular solids in which the isolated Fe granules are only nanometers in size. Across the whole volume fraction range magnetic coercivity experiences dramatic variations due to the change of granular size and percolation effects.

Magnetic granular solids are a special artificial metallic system consisting of ultrafine ferromagnetic particles embedded in an insulating matrix such as an oxide. With dimensions in the nanometer range, the small particles exhibit unusual properties with diverse technical applications.[1-3] Inherent to granular metal systems is the phenomenon of percolation. The percolation threshold (p_c), above which a connecting network of granules exists, is usually near a metal volume fraction (p) of about 60%.[1] Across p_c dramatic changes in various properties occur, and of those the electrical conductivity is perhaps the most obvious.[1] In this work, we report the observation of giant magnetic coercivities and a strong percolation effect realized in a magnetic granular system. Bulk Fe generally has a coercivity less than 50 Oe. In our granular Fe-(SiO_2) solids, magnetic coercivities as high as 2500 Oe have been found. The results presented here are of a general nature and should be applicable to other magnetic granular systems.

The granular Fe-(SiO_2) samples were fabricated by using a high-rate rf magnetron sputtering system. The sputtering targets were made from homogeneous mixtures of pure Fe and SiO_2. The presputtering pressure in the vacuum chamber was about 1×10^{-8} Torr. Great care was taken in maintaining constant sputtering conditions, such as sputtering rate and pressure of the Ar plasma, to assure a uniform size of the ultrafine granules. The samples, with thickness of 2–5 μm, were deposited onto Kapton substrates kept at room temperature. The composition of the samples was cross checked with atomic absorption, x-ray fluorescence analysis, and target composition, with general agreement within 5 at. %.

We have made granular Fe-(SiO_2) solids over a large Fe volume fraction range (p) from 15% to 100%. The microstructures of the samples were examined by transmission electron microscopy (TEM), as well as electron and x-ray diffraction. Examples of the TEM micrograph are shown in Fig. 1, where the structures of two samples, $Fe_{90}(SiO_2)_{10}$ and $Fe_{60}(SiO_2)_{40}$, with respective Fe volume fractions of 70% and 29% (which are above and below the percolation threshold), are clearly displayed. The $Fe_{90}(SiO_2)_{10}$ sample consists of large connecting granules, while the small Fe granules are well separated in $Fe_{60}(SiO_2)_{40}$. Electron diffraction established that the granules have a bcc structure, the same as α-Fe. Further confirmation came from ^{57}Fe Mössbauer spectroscopy. With room-temperature substrates, we observed a monotonic increase of granule size with Fe volume fraction. Specifically we obtained average granule sizes of 17, 38, 50, and 70 Å for samples with $p = 14\%$, 29%, 38%, and 70%, respectively. These approximately equiaxial granules exist in magnetic single domain form because their sizes are smaller than the critical size for single domain Fe particles ($\sim$200 Å).[4]

Magnetic measurements were performed by using a superconducting quantum interference device magnetometer with a field range of 0–50 kOe and a temperature range of 2–400 K. The planes of the granular films were parallel to the external field to minimize demagnetization effects. The magnetic coercivity was determined from either a complete or a portion of a hysteresis loop with magnetic fields up to 50 kOe. Measurements were made at various temperatures up to 400 K. In order to study the ground-state properties, measurement at 2 K was always included.

A typical magnetic hysteresis loop of a Fe-(SiO_2) granular film ($p = 42\%$) measured at $T = 2$ K is shown in Fig. 2, from which the coercivity (H_c) and the squareness (Mr/Ms) can be readily extracted. For an assemply of non-

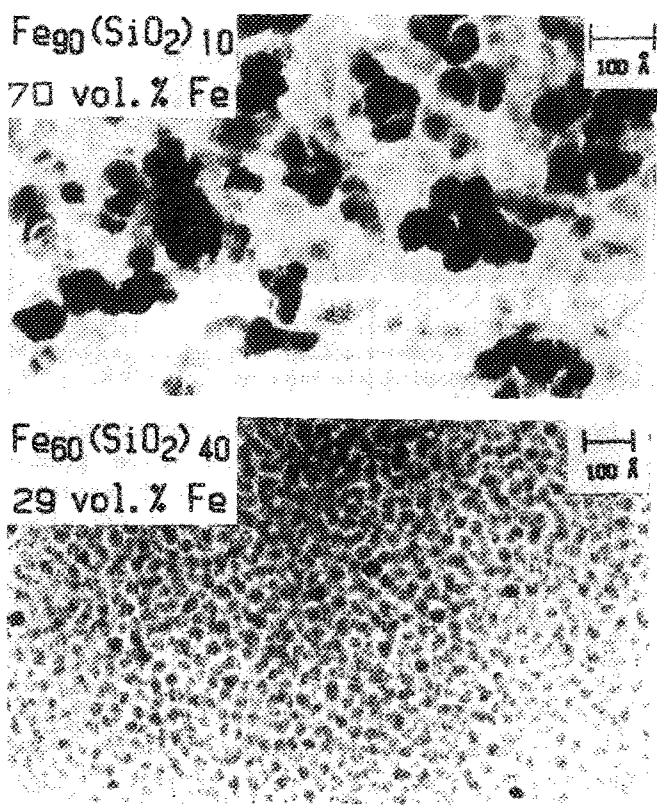

FIG. 1. TEM micrograph of granular $Fe_{90}(SiO_2)_{40}$ (70 vol % Fe) and $Fe_{60}(SiO_2)_{40}$ (29 vol % Fe) films.

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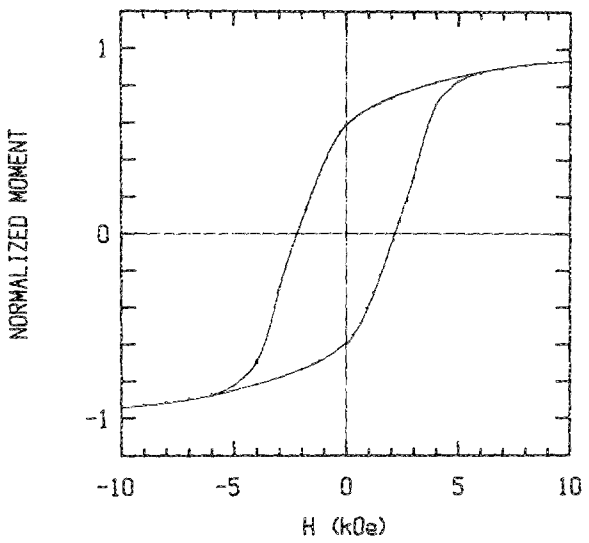

FIG. 2. Magnetic hysteresis loop of an Fe-SiO_2 granular film with Fe volume fraction of 42% ($T = 2$ K).

interacting particles with randomly distributed magnetic easy axes, the statistical average of Mr/Ms at $T = 0$ K is exactly 0.5.[4] This has been observed in our samples with $p < 29\%$. For samples with higher p values ($p > 30\%$) but below p_c, the squareness is slightly larger than 0.5. For example, the sample ($p = 42\%$) in Fig. 3 has a value of $Mr/Ms = 0.60$. These slightly larger squarenesses are caused by the increasing magnetostatic interaction among particles as p increases. Such observations are consistent with a mean field calculation by Bertram and Bhatia.[5]

In Fig. 3, the H_c data of the Fe-(SiO_2) system at 2, 77, and 300 K are presented as a function of the Fe volume fraction p. The results at 2 K are close to the ground-state properties, in which one observes a giant enhancement of H_c. Keeping in mind that H_c of bulk Fe is less than 50 Oe due to magnetic multidomain structure, we find that the granular Fe sample has a H_c as high as 2500 Oe. There are a number of distinctive features in H_c as the volume fraction (p) is increased. Starting from the low p side, H_c increases slowly until $p = 29\%$ where it experiences a fivefold increase, reaching a peak of 2500 Oe at $p = 46\%$. Then it precipitously drops to a value of about $H_c \sim 50$ Oe, which is close to the value of the sputtered bulk pure Fe, and remains at that value from $p = 60\%$ to 100%. Spectacular changes in H_c occur in the region of $29\% \leqslant p \leqslant 60\%$, where the upper limit in p coincides with the percolation threshold of $p_c \sim 60\%$ as obtained from electrical conductivity studies of various granular solids.[1]

The precipitous decrease in H_c is attributed to the percolation effect. As p approaches the percolation threshold, formation of a connecting network of small granules starts to occur. Under such conditions, the granules would prefer a magnetic closure-domain structure[4] due to dipolar interaction, and effectively the system behaves like a multidomain structure even though individual particles still remain single domain. As a result, magnetic coercivity reduces substantially.

As shown in Fig. 3, H_c decreases as temperature increases. This is because thermal agitations at elevated temperature tend to destabilize the magnetic moments of the single-domain particles. According to Kneller and Luborsky,[6] the temperature dependence of coercivity for noninteracting uniform particles is

$$H_c = H_{co}(1 - \sqrt{T/T_g}), \tag{1}$$

where T_g is the onset temperature for superparamagnetism which is proportional to the magnetic anisotropy energy KV, with K being the anisotropy constant and V the granular volume. The values of H_c of three samples ($p = 36.8\%$, 39%, 41.4%) have been measured between 2 and 350 K. In Fig. 4, H_c in reduced units are plotted as a function of $\sqrt{T}$. For a sample with low p (e.g., $p = 36.8\%$), the $\sqrt{T}$ dependence is observed. For samples with larger p values, $\sqrt{T}$ pro-

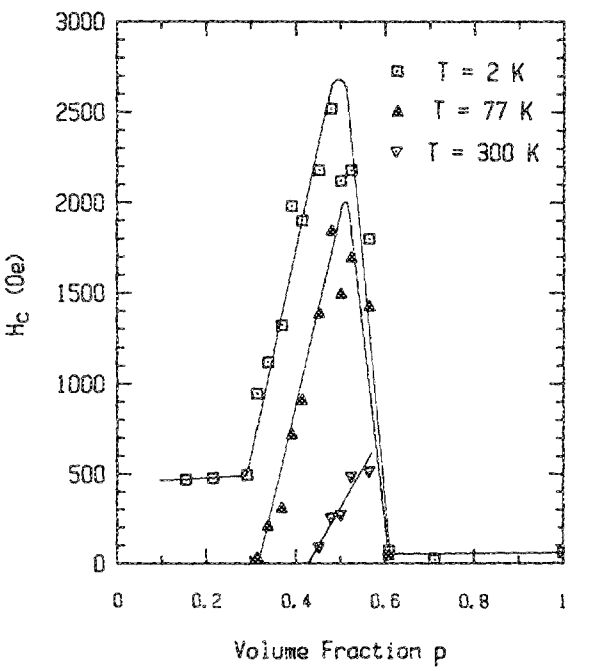

FIG. 3. Magnetic coercivities measured at $T = 2$, 77, and 300 K of Fe-SiO_2 granular films as a function of Fe volume fraction.

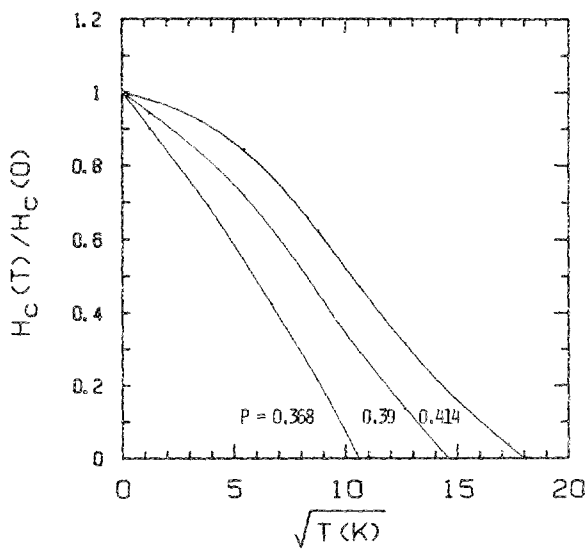

FIG. 4. Temperature dependence of the normalized coercivity for samples with $p = 36.8\%$, 39%, and 41.4%.

vides an adequate description but with some noticeable deviations possibly due to a broader size distribution. The temperature at which H_c vanishes, according to Eq. (1), gives the value of T_g which is a measure of KV.

For samples deposited at room temperature, larger particle sizes are realized in samples with higher values of p as mentioned earlier. This would normally result in a stronger dipole-dipole interaction, which tends to decrease H_c as established both theoretically[7] and experimentally.[8] Therefore, the observed increase of H_c must be associated with the effects due to the increase of particle size. This indeed is supported by the following experiment. We deposited three samples with the same volume fraction (29%) at three different temperatures 30, 200, and 400 °C. The high substrate temperature effectively enlarges the particle size. The respective H_c for these three samples are 490, 810, and 1500 Oe, indicating the scaling of H_c with particle size.

There are two anomalies in the behavior of H_c in the granular Fe-SiO_2 system. First, the experimental results establish that H_c increases dramatically with particle size. Such a phenomenon, observed at 2 K, is not a thermal artifact due to magnetic relaxation,[6] but intrinsic to Fe-SiO_2. The second is the extremely high H_c values (at least 2500 Oe) achieved in the granular system.

According to conventional theories,[9] for Fe particles with sizes less than 120 Å, the rotation-in-unison mode of magnetization reversal is more favorable than bucking and curling modes. In this mode, the zero-temperature coercivity H_{co} is $2K/M$, where M is the magnetization and K is the effective anisotropy constant from various contributions such as magnetocrystalline, shape, strain, etc.,[4] which are largely independent of size. Since the magnetization remains relatively constant in our Fe-SiO_2 system, the effective K would necessarily be size dependent in order to account for the experimental results. Further difficulties are encountered when very large H_c values are to be accommodated in various models. Both the magnetocrystalline anisotropy and the maximum strain induced coercivity of bulk Fe are only of the order of 600 Oe.[4] In the rotation-in-unison model, H_c was predicted to be as high as 5000 Oe but only for particles with an extremely large aspect ratio.[4] The chain-of-spheres fanning model[10] indicates a maximum H_c of 2700 Oe for an infinitely long chain in a random system. These extreme particle shapes and morphology were not revealed in our TEM micrographs. We are therefore led to the conclusion that the observed anomalies of H_c in granular Fe-SiO_2 cannot be satisfactorily accounted for by existing models.

However, it must be recognized that the above-mentioned models, and indeed almost all the existing models, assume free-standing particles or particles dispersed in a nonbonding medium. In the granular Fe-SiO_2 system, the particles are strongly bonded to the insulating matrix and may be subjected to very larger stresses. For small particles, a large portion of the Fe atoms are at or near the surface. The number of surface atoms increases with particle size. The metal-insulator interfaces may dominate the coercivity in such systems. Under a reversing field, the moment reversal may well begin first at the surface and then propagate throughout the particle.

In summary, granular Fe-SiO_2 solids exhibit a giant magnetic coercivity which peaks at 46% metal volume fraction with a value of 2500 Oe. At higher volume fractions, H_c drops to the bulk Fe value due to the percolation effect. At the low volume fraction side, there is a fivefold increase in H_c due to increasing particle size. The results cannot be fully accounted for by the existing models of small particles which neglect the importance of surface states between the metal particles and the bonding insulating matrix.

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