

Structural and magnetic properties of ultrafine Fe-Pd particles

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The structural and magnetic properties of evaporated ultrafine Fe-Pd particles have been studied near the equiatomic composition. Particles with an average size in the range of 65–360 Å were obtained with the argon pressure varied between 0.5–40 Torr. All of the as-made particles had a face centered cubic (fcc) structure and they were magnetically soft. A fcc to face centered tetragonal (fct) phase transformation was observed after annealing the powders at 500 °C resulting in room-temperature coercivities up to 3.6 kOe and a magnetization (at 55 kOe) around 95 emu/g. An enhanced magnetic moment of about $3.0\mu_B$ per atom was found for Fe.

I. INTRODUCTION

Fe-Pd alloys have been of special scientific interest because the Fe atoms induce a large host polarization leading to an overall enhancement in the magnetic moment.^{1,2} According to the equilibrium phase diagram of $\text{Fe}_{1-x}\text{Pd}_x$ alloys,³ below 1000 °C an Fe-rich bcc phase is expected for $0 < x < 0.2$, a bcc-fcc mixed phase for $0.2 < x < 0.45$, and an fcc phase for $x > 0.45$. There are two ordered-disordered phase transformations in these alloys; one to the FePd face centered tetragonal (fct) phase near the 50% Pd composition and another to FePd_3 face centered cubic (fcc) phase in the range of 62.8%–74.4% Pd. The ordered fct phase is a hard magnetic phase because of its high anisotropy.⁴ In Fe-Pd thin films no superlattice structure was detected for the concentration regions around 50% Pd and 75% Pd.⁵

Magnetic ultrafine particles in the nanometer scale prepared by evaporation are very easy to burn and need a protective coating to resist oxidation when exposed to the ambient. The magnetic properties of ultrafine particles are mainly influenced by the size of the particles and by the surface layer of the properties.^{6,7}

In this paper we studied the size effects on the magnetic and structural properties of Fe-Pd ultrafine particles with both the fcc and fct structures.

II. EXPERIMENTAL METHODS

Bulk Fe-Pd alloys were made by arc-melting high-purity Fe and Pd metals in an argon atmosphere. Ultrafine Fe-Pd particles (UFP) were produced by gas evaporation and condensation of a piece of bulk $\text{Fe}_{100-x}\text{Pd}_x$ in an argon atmosphere. A tungsten crucible was used as the heating element. Control of the particle size was obtained by varying the argon pressure from 0.5 to 40 Torr during evaporation. The particles were passivated with an Ar/air mixture before they were taken out from the evaporation chamber. Then they were annealed under vacuum (10^{-5} Torr) at temperatures in the range of 400–800 °C.

The composition of the particles was determined by ICP spectroscopy. The magnetic properties were measured by a superconducting quantum interference device (SQUID) and

vibrating sample magnetometer (VSM) with applied fields up to 55 kOe. The particle structure and morphology were examined by x-ray diffraction (XRD) and transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSION

The average particle size D was found to depend on the argon gas pressure during evaporation, increasing monotonically with increasing argon pressure. Because of the different vapor pressures of iron and palladium the particle composition was found to be slightly dependent on the evaporation pressure (Table I), with a lower Fe content obtained at higher Ar pressure. The Fe content of evaporated powders was in the range of 44–51 at % when a master ingot of $\text{Fe}_{45}\text{Pd}_{55}$ was used.

X-ray diffraction patterns showed that all the as-made particles have a face centered cubic (fcc) structure [Fig. 1(a)]. With increasing Ar pressure the (111) diffraction peak is shifted to smaller angles indicating an increase in the lattice parameters (Table II). This change of lattice parameter is the result of a composition change, where a larger lattice parameter means a higher percentage of palladium. However, ICP composition analysis data showed a lower Pd percentage in the smaller particles. These contradictory results are due to the fact that the ICP composition analysis data represent the entire particle composition while the x-ray diffraction shows only the structure of the fcc Fe-Pd major phase. We believe that a small amount of Fe-O forms on the particle surface leaving an Fe-Pd core with an Fe content below the equiatomic composition. The smaller particles have a larger surface area, which results in an inhomogeneous FePd composition distribution.

TABLE I. Composition as a function of Fe-Pd particle size.

Composition	Average particle size (Å)			
Ingot	65	135	230	360
$\text{Fe}_{45}\text{Pd}_{55}$	$\text{Fe}_{51.6}$	$\text{Fe}_{49.7}$	$\text{Fe}_{47.8}$	$\text{Fe}_{44.2}$
	$\text{Pd}_{48.4}$	$\text{Pd}_{50.3}$	$\text{Pd}_{52.2}$	$\text{Pd}_{55.8}$

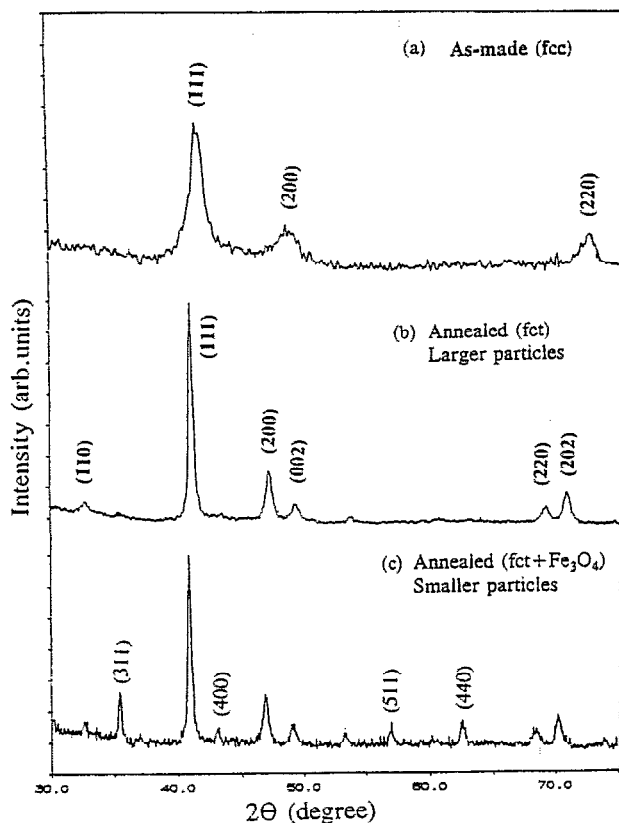


FIG. 1. X-ray diffraction patterns in Fe-Pd particles.

The x-ray diffraction peaks were weak and broad in the as-made samples and sharp in the annealed samples. The sharper peaks indicate larger particles. TEM pictures showed that the particle size is consistent with the x-ray diffraction results. The as-made spherical particles had an average size in the range of 65–360 Å corresponding to an Ar pressure between 0.5–40 Torr. After heat treatment the average particle size increased to 115–430 Å. The heat treatment also led to sintering of the smaller particles (Fig. 2).

The fcc to face centered tetragonal (fct) phase transformation was observed in the larger particles after a suitable heat treatment. X-ray diffraction patterns showed clearly the superlattice reflections of fct (002), (202), [Fig. 1(b)], with a trace of Fe_3O_4 present in the particles. The Fe_3O_4 x-ray dif-

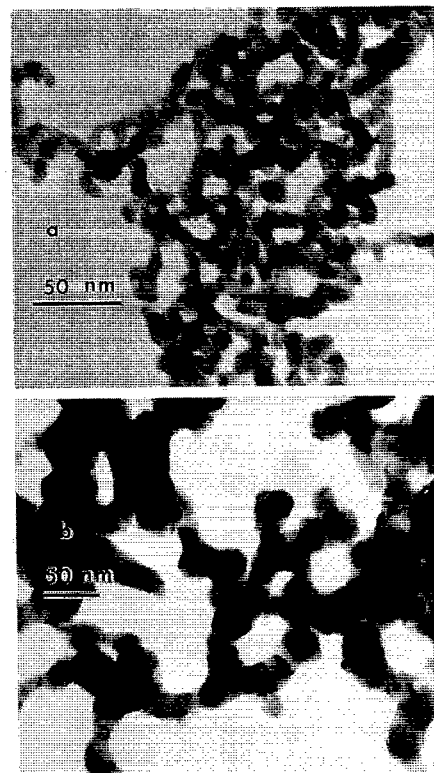


FIG. 2. Fe-Pd particle morphology, (a) as-made, (b) annealed.

fraction peaks are stronger in the annealed smaller particles [Fig. 1(c)] indicating an increase in both the amount and grain size of the oxides. No phase transformation was observed in the as-made particles with a size below 100 Å. This result is consistent with the core-shell morphology picture where the composition of the Fe-Pd core in the smaller particles deviates from the equiatomic range. In order to obtain equiatomic FePd core in the smaller particles the composition of the master alloy had to be shifted toward the Fe-rich range. Table II(b) shows the lattice parameters of the smaller particles with a size below 100 Å. An attempt was made to eliminate the surface oxidation by sandwiching the smaller

TABLE II. Lattice parameters of Fe-Pd particles.

Composition of master ingot	Particle size (Å)	Lattice parameter a (Å)	Composition Fe (at %)
$\text{Fe}_{45}\text{Pd}_{55}$	360	3.822	44.2
	310	3.810	...
	230	3.806	47.8
	180	3.806	...
	135	3.804	49.7
$\text{Fe}_{55}\text{Pd}_{45}$	90	3.852	...
	65	3.881	51.6
	90	3.805	52.5
$\text{Fe}_{65}\text{Pd}_{35}$	75	3.801	59.14

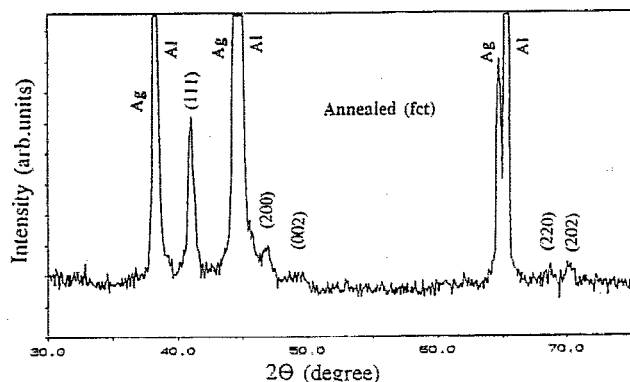


FIG. 3. X-ray diffraction pattern of Ag/FePd/Ag sandwiched particles (80 Å). The Al peaks come from the Al foil substrate.

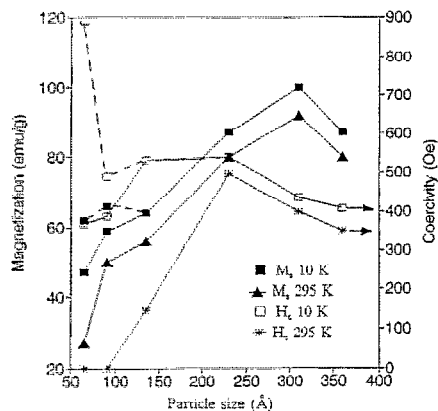


FIG. 4. Magnetic properties of as-made Fe-Pd particles, (—) nominal $\text{Fe}_{45}\text{Pd}_{55}$, (---) with adjusted composition.

particles between two Ag thin films. After annealing, the sandwiched FePd particles with 80 Å size show the fct phase when an $\text{Fe}_{45}\text{Pd}_{55}$ master alloy was used (Fig. 3). This evidence supports the predicted particle morphology which influences the structural properties.

The magnetization of the as-made particles was found to be highly dependent on particle size (Fig. 4). The magnetization increases with particle size to the maximum value of 100 emu/g obtained in a sample with a size around 300 Å. The decrease in magnetization observed in the larger particles is due to a change in particle composition towards higher Pd content. The lower magnetization of smaller particles in the nominal $\text{Fe}_{45}\text{Pd}_{55}$ (solid line) and adjusted * composition samples (dashed line) is probably due to both surface oxidation and the Pd-rich core phase effects. The magnetization of annealed samples does not show much dependence on particle size (Fig. 5), and its value is close to that of Fe-Pd thin films.⁵

In fine Fe-Pd particles with both the fcc and fct phases, the magnetization value per Fe is obviously higher than 220 emu/g. Table III shows the magnetic moment of the samples. The samples with the asterisk (*) are those prepared from Fe-rich-Pd alloys. The moments decrease with decreasing particle size. The magnetization of the larger particles is

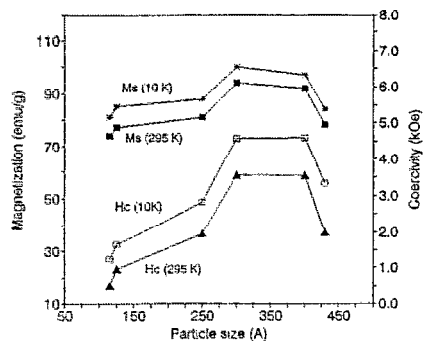


FIG. 5. Magnetic properties of annealed Fe-Pd particles (fct).

TABLE III. Magnetic moment of annealed Fe-Pd particles (fct) at 10 K.

As-made size (Å)	Fe (at %)	K (erg/cm ³) $\times 10^{-6}$	μ_B (Fe) as-made	μ_B (Fe) H.T.
360	44.2	2.3	2.97	2.86
230	47.8	3.65	2.68	3.08
135	49.7	2.59	1.87	2.58
90*	52.5	1.96	2.26	2.32
75*	59.14	1.69	1.46	1.88

close to that of bulk samples.⁸ The moments are slightly different in the annealed samples and this is probably due to differences in the magnetization values of the fcc and fct phases and to a different Fe-O content in the samples.

The as-made powders had a coercivity in the range of 0–500 Oe which was dependent on particle size. The coercivity in the 65–90 Å particles was zero at room temperature, and increased with particle size reaching a maximum value of 500 Oe around 230 Å particles, and then it decreased again in larger particles. A different behavior has been observed at 10 K for particles with size below 200 Å. The largest coercivity has been obtained in the 75 Å particles and this behavior is similar to that of Fe/Pd and Fe-Cr particles and is believed to be the result of the FePd core/Fe-O shell particle morphology. After annealing, the samples with the fct structure had much higher coercivities (Fig. 5) with a maximum coercivity 3.56 kOe at 295 K corresponding to a particle size around 280 Å. The behavior of the coercivity as a function of size is similar to that of as-made powders. The estimated single domain particle size for equiatomic FePd is about 350 Å.

IV. SUMMARY

In the larger Fe-Pd particles the magnetic moments and the phase transformation behavior are close to those of bulk. The magnetization and coercivity of these particles are mainly governed by the FePd core phase (both fcc and fct). In the smaller particles, however, a larger lattice parameter and a trace of Fe_3O_4 indicate a particle morphology with an Fe-Pd-rich core surrounded by an Fe-O shell which we believe affects the fcc to fct phase transformation and the magnetization of the particles.

ACKNOWLEDGMENT

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