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Synthesis and structural, magnetic and magnetotransport properties of permalloy powders containing nanoparticles prepared by arc discharge

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ABSTRACT

We report the synthesis of permalloy powders that were made using an arc-discharge method and with 78% or 45% Ni concentrations in N_2 or Ar. Our research was motivated by the fact that magnetic nanoparticles displaying large magnetoresistances are useful for magnetic field sensors applications. The permalloy powders contained some nanoparticles and the particle sizes ranged from 10 nm to ~20 μm. The highest quality powders were made using a 78% Ni permalloy rod in N_2 where the coercivity was low (0.3 mT) and the saturation moment per formula unit was slightly less than that expected for the bulk compound. Magnetoresistance was observed in a cold pressed pellet where it is likely to be dominated by the ordinary magnetoresistance and spin-dependent tunneling between the particles.

1. Introduction

There is considerable interest in magnetic nanoparticles because of the range of potential applications that include magnetic data storage [1], magnetic field sensors [2], and magnetic resonance imaging contrast agents [3]. The use of magnetic nanoparticles is particularly attractive especially if they display electronic spin polarization where spin tunneling can lead to a large magnetoresistance (MR) [4–8] and hence they can be used as MR magnetic field sensors. If the nanoparticles are small enough then they can also be superparamagnetic. This occurs when the thermal energy is greater than the magneto-crystalline anisotropy energy, K_{eff}. There is no hysteresis for temperatures above the blocking temperature that can be defined as $T_B = [K_{eff}(4\pi r^3/3)]/[25k_B]$ where r is the nanoparticle radius and k_B is Boltzmann's constant [9]. This is very advantageous for low field MR magnetic field sensors because the presence of magnetic hysteresis means that low magnetic fields cannot be measured unless a bias magnetic field is applied [2]. Hysteresis is also a problem with fluxgate magnetometers where moderate magnetic fields lead to a remnant magnetization in the core that can affect the sensitivity.

The need for better MR magnetic field sensors, where the sensitivity is not affected by moderate magnetic fields, has motivated our research into magnetic nanoparticles [8,9]. Permalloy is one compound that can potentially be used because K_{eff} can be very small [10], which results in a small saturation field [11]. It also displays electronic spin polarization [4] and hence granular or cold pressed powder samples should display spin tunneling MR [12]. Permalloy nanoparticles have been made by methods that include radio frequency plasma torch synthesis [13], magnetron sputtering [14], pulsed laser ablation [15], polyol processing [16], and using a microemulsion method [17]. In this paper we report the synthesis and characterization of magnetic permalloy powders fabricated using a new and relatively simple arc-discharge method. This method has only previously been used to fabricate nonmagnetic nanoparticles [18].

2. Methods

Permalloy powders were synthesized using the arc-discharge system at GNS Science [18]. A permalloy rod was the anode and the cathode was Fe that sat on a water-cooled graphite disc. The cathode and part of the anode were surrounded by a metal shield that sat on the graphite disc. Peramalloy-45 and permalloy-78 were used. Permalloy-45 (P45) contained 45% Ni and the remainder was predominately Fe with low concentrations of Mo, C and Mn. Permalloy-78 (P78) contained 78% Ni and the remainder was predominately Fe with low concentrations of Mo, C and Mn. The anode and cathode were located inside a sealed chamber. The arc-discharge was carried out using a current of 74 A and maintaining a gap of

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~5 mm between the electrodes. The syntheses were performed in nitrogen or argon at a pressure of ~400 Torr. Two different atmospheres were used to see if the atmosphere affects the resultant composition. The powder was collected inside the base of the metal shield after arc-discharge. Some of the powder from the P78 sample made in N_2 was cold pressed into a 3 mm diameter pellet at a pressure of 14 MPa for MR measurements.

The structural properties were studied by X-ray diffraction (XRD) using Cu Kα radiation, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). Magnetic measurements were made using a magnetic property measurement system (MPMS) from Quantum Design. Magnetoresistance measurements were made using the four-terminal method in a Quantum Design PPMS and with the current parallel or perpendicular to the applied magnetic field. The four-terminal MR measurements were made by first evaporating silver electrodes and then using silver epoxy bonded contact wires.

3. Results and discussion

XRD data from the P45 and P78 powders after arc-discharge in nitrogen or argon are shown in Fig. 1. The XRD peak positions are consistent with face centered cubic (FCC) $Ni_{1-x}Fe_x$ where the space group is Fm3m. There is no evidence for body centered cubic Fe (space group Im3m) in any of the powders. There is also no evidence for other phases in the P78 powder made in N_2, while the P78 powder made in Ar contains some impurity phases. Impurities are clearly seen in the P45 powders and the P45 powder made in N_2 contains split peaks that indicate 2 permalloy phases. The impurity peaks are due to phases containing Mo, Mn, Fe, Ni and their oxides.

The lattice parameter was obtained for all of the powders from the XRD data and it is listed in Table 1. The P78 powders have a lattice parameters, a, that are intermediate between that expected for Ni (3.5236 Å) and Fe (3.6468 Å). It is also close to that expected for permalloy for a similar concentration where $a = 3.5556$ Å [19]. Thus, the lattice parameters are consistent with the powders containing permalloy. The lattice parameter for P45 made in Ar is higher and based on a simple linear interpolation of the Ni and Fe lattice parameter, it would be expected that a is ~3.58 Å, which is close to the observed value. Therefore, P45 made in Ar contains a significant fraction of permalloy with a Ni content close to that of the starting material. The P45 powder made in N_2 has split FCC peaks that indicate 2 phases where the lattice parameters are close to that expected for P45 and P78.

SEM measurements show that all of the powders have a range of particle sizes. This is evident in Fig. 2 (upper figure) that shows a typical SEM image of the P78 powder made in N_2, where it can be seen that the particles sizes extend up to ~20 μm. There are also some nanoparticles in the powders as can be seen in the HRTEM image in Fig. 2 (left figure) of P78 made in Ar. The particle size distribution for this powder was obtained from a HRTEM image and it is shown in the lower right of Fig. 2. The particle size distribution is typical of that seen for all of the powders where there are some small nanoparticles but the particle size distribution extends beyond 50 nm, which is the upper limit of nanoparticle size that could be observed by HRTEM. 50 nm is conveniently also the critical radius for observing superparamagnetism at 300 K. This can be shown from $T_B = [K_{eff}(4\pi r^3/3)]/[25k_B]$ and taking $T_B = 300$ K and using the measured magnetocrystalline anisotropy energy of 200 Jm^{-3} for quenched P78 [10]. Thus, there are some crystalline nanoparticles with radii less than the critical superparamagnetic radii (50 nm) although there is a wide particle size distribution that extends up to ~20 μm.

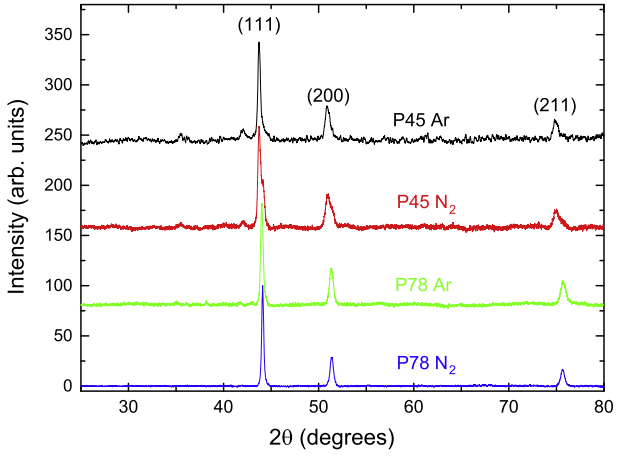

Fig. 1. XRD data from P45 and P78 made in Ar or N_2. The data are offset for clarity and normalized to the same (111) peak intensity.

Table 1
Table of the lattice parameter, the saturation moment per formula unit at 5 K, and the coercive fields at 300 K for P45 and P78 made in different gases.

Sample code	Gas	Lattice constant (Å)	m_s/μ_B	$\boldsymbol{B}_c$ (mT)
P45	N_2	3.582 and 3.55	1.30	0.7
P45	Ar	3.583	1.48	0.5
P78	Ar	3.559	0.78	1.6
P78	N_2	3.553	0.74	0.3

The magnetization data from the P78 powder made in N_2 is plotted in Fig. 3 against the applied magnetic field at 5 K and 300 K. The saturation magnetization is only slightly lower at 300 K, which indicates that the Curie temperature is far above room temperature. The saturation moment per formula unit, m_s/μ_B, is 0.74, which is in-between that expected for Fe ($m_s/\mu_B = 2.2$ [20]) and Ni ($m_s/\mu_B = 0.62$ [20]). It is also slightly less than that expected for bulk permalloy with a similar Ni concentration (m_s/μ_B ~0.95 [21]). It is apparent in the insets to Fig. 3 that there is some hysteresis at 5 K and 300 K. This is expected because most of the particles are greater than 50 nm and hence the hysteresis arises from these non-superparamagnetic particles. The coercive field is low at 300 K and it is 0.3 mT. This is consistent with permalloy that has Ni concentrations comparable to P78 because K_{eff} is small [10,22].

Magnetization measurements were done on the other powders and the resulting saturation moments and coercive fields from all of the powders are listed in Table 1. It can be seen that m_s/μ_B is similar for P78 made in Ar or N_2 and consistent with permalloy with similar Ni concentrations. P45 made in Ar has a larger m_s/μ_B, which is expected for a larger Fe fraction. However, m_s/μ_B is lower for P45 made in N_2. This is due to the 2 permalloy fractions that are close to P45 and P78.

Magnetoresistance measurements were performed on a P78 pressed pellet made in N_2 and the results are shown in Fig. 4 at 5 K and 300 K for the current parallel or perpendicular to $\boldsymbol{B}$. The MR is defined as $MR(\boldsymbol{B}) = (R(\boldsymbol{B}) - R(0))/R(0)$ where $R(\boldsymbol{B})$ is the resistance for an applied magnetic flux density, $\boldsymbol{B}$, and $R(0)$ is the resistance when $\boldsymbol{B} = 0$. This powder was chosen because there was no evidence of impurity phases in the XRD data. There is a small dip in the MR below 20 mT of unknown origin. It is also observed at 300 K and hence it is unlikely to be due to a quantum MR.

For $\boldsymbol{B} > 20$ mT, the MR at 5 K decreases with increasing $\boldsymbol{B}$ until $\boldsymbol{B} \sim 1.5$ T after which the MR increases. It is also apparent that the MR depends on the angle between the current and $\boldsymbol{B}$. $Ni_{1-x}Fe_x$ alloys are known to display an anisotropic magnetoresistance (AMR) that arises from s–d scattering and the spin–orbit interaction that leads to scattering between spin-up and spin-down carriers [23–27]. This results in a resistivity in polycrystalline samples of the form [23],

$$\rho(\vartheta) = \rho_{perp} - [\rho_{para} - \rho_{perp}] \times [\cos(\vartheta)]^2 \quad (1)$$