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Observation of enhanced positive magnetoresistance at low temperatures in $Ni_{0.8}Fe_{0.2}$/C granular composites

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ABSTRACT

$(Ni_{0.8}Fe_{0.2})_xC_{100-x}$ (x = 0–50%) granular compositions were prepared using mechanically alloyed nanocrystalline NiFe powders and graphite. Magnetic measurements and structural data on mechanically alloyed samples show the presence of dominant NiFe phase along with fcc-Ni phase. All the samples exhibit positive magnetoresistance (MR) in the whole temperature range and applied field range of present study. The analysis of the magnetization and MR data suggests that large positive MR could be due to the graphite matrix rather than magnetic particle contribution.

1. Introduction

It is now well established that there exists a relation between the giant magnetoresistance (GMR) and spin-dependent scattering at the interfaces in magnetic/non-magnetic multilayers [1]. However, in the case of discontinuous multilayers and heterogeneous alloys/granular materials in which magnetic entities are (Co, Fe, Ni and their alloys) dispersed in a metallic non-magnetic matrix (Cu, Ag), the actual mechanism for observation of GMR is yet to be established [2–7]. In a system, where fine ferromagnetic/superparamagnetic particles are embedded in a non-magnetic matrix, negative GMR has been observed, which is attributed to spin-disorder scattering of electrons either within or at the interfaces of the magnetic particles dispersed throughout the non-magnetic matrix [1–3]. In this case, the magnetic particle moments are randomly oriented and the resistivity of the material is higher than when they are aligned by the application of an external magnetic field. Granular alloys, which exhibit GMR, are usually obtained by mixing two immiscible materials, one magnetic and the other is non-magnetic, resulting in formation of magnetic particles embedded in a non-magnetic matrix [3]. The magnitude of the magnetoresistance (MR) depends on both size and the concentration of the magnetic entities in the alloy. This effect has been postulated to be due to the existence of an optimum particle size, determined by the conduction electron mean free path and is also due to the percolation, which acts to couple the particles ferromagnetically [2,7]. In addition to this, the matrix too has its role in regulating the magnetic and electrical transport behavior. For non-magnetic metals, semimetals and semiconductors, the MR is usually negligible at 300 K at low magnetic fields [8–10]. However, narrow gap semiconductors, heavily disordered semiconductors exhibit a linear response to the magnetic field [11,12]. Such linear behavior is known to occur in an isotropic medium with a low volume fraction of insulating inclusions, but linearity holds good for only very high fields. Therefore, metal matrix systems, such as, Co–Cu, Ag–Fe and insulator matrix systems, such as, $Fe–In_2O_3$, $Co–SiO_2$ have been investigated by various groups [13–16]. In the metal matrix systems, the inter-particle magnetic interactions are mediated through the conduction electron, while in insulating matrix this possibility is considerably reduced which affects the magneto-transport behavior. However such studies with less conducting materials or insulating/semiconducting non-magnetic materials would reveal the role of interaction effects in the GMR phenomenon. It is now realized that the dilute magnetic semiconductors are good candidates for spintronics applications. Therefore, transition-metal (TM) elements and rare-earth (RE) metal elements are doped in semiconductor matrix to achieve higher MR values [17]. Interestingly enough TM-RE codoped polycrystalline In_2O_3 shows giant positive MR values (85% at T = 2 K) at low temperatures but drops down to very small values as the temperature is raised [15]. Similar behavior was also observed in self-assembled Co@CoO nanoparticle arrays at temperature below 100 K [10], in non-magnetic silver chalcogenides [9], perovskite type manganites and inhomogeneous narrow gap semiconductors [11].

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On the other hand, remarkable positive MR of ∼59% at 300 K under 80 kOe magnetic field and 105% under 50 kOe at 5 K have been reported in $Co_{10}C_{90}$ compacts [4]. Other transition metals in graphite matrix have also been investigated and all the compacts show higher positive MR values. For example, $Fe_{20}C_{80}$ exhibits ∼54% and 190% MR at 300 and 5 K respectively under a magnetic field of 50 kOe [5], while $Ni_{20}C_{80}$ exhibits ∼44% and 138% MR at 300 and 5 K, respectively [6]. Badia et al. reported ∼21% negative MR in a magnetic field of 12 kOe at 21.5 K in annealed $Fe_{7.6}Ni_{16.4}Ag_{76}$ samples [1,3]. But heat treated $(Fe_{20}Ni_{80})_{21}Ag_{79}$ thin films showed only 6% MR at 300 K and 13% at 77 K in ∼8 kOe magnetic fields [7]. $Fe_{8.7}Cu_{91.3}$ granular thin films also exhibit ∼13% negative MR at 3 K on applying of 50 kOe magnetic field [18]. Nanometer sized permalloy ($Ni_{0.8}Fe_{0.2}$) particles embedded in graphite matrix showed large (∼26%) positive MR at 300 K under a magnetic field of 50 kOe [19]. On the basis of the magnetic and MR investigations, Mandal et al. [19] suggested that significant contribution to the MR stems from the graphite matrix at 300 K where the MR characteristics have been explained on the basis of the semi-metallic nature of the graphite matrix. Such an argument seems to be realistic at room temperature due to the presence of relatively large number of charge carriers. But it remains to be seen what happens to MR at lower temperatures, as the number of carriers available for the conduction would reduce in number. However, the low temperature MR studies on these composites have not been reported. Further, earlier studies focused on transition metal–graphite (C) composites but the role of graphite matrix has not been investigated systematically at low temperatures. We believe that the low temperature MR can provide insight into the role played by matrix and magnetic entities. On the other hand, the annealing time shows strong effect on the sign and magnitude of the MR [20]. The aim of the present work is to see how MR varies with temperature? Whether the temperature dependence is similar to that observed in several granular alloys where non-linear effects dominate at lower temperatures? Whether matrix or magnetic component plays a major role in enhancing the MR values? To seek answers to some of these questions, here we report a comprehensive study on $Ni_{0.8}Fe_{0.2}$ (permalloy composition) fine particles dispersed in graphite matrix. Magnetic and magnetoresistance behavior of the composites has been investigated in order to investigate the role of magnetic component in observation of large positive values of MR in graphite-permalloy composites at low temperatures.

2. Experimental details

Mixtures of appropriate amounts of Fe (<10 μm, 99.9+ %) and Ni (200 mesh, 99.9%) powders corresponding to the nominal compositions of $Ni_{0.8}Fe_{0.2}$ were mechanically alloyed using a planetary ball mill (RETSCH-PM 200) with tungsten carbide milling media in toluene atmosphere up to 60 h. Toluene has been taken as lubricant and coolant during milling to avoid the oxidation effect. The ball to powder ratio (BPR) was 10:1. As milled powders of $Ni_{0.8}Fe_{0.2}$ (abbreviated as FN in future discussion) were thoroughly mixed by mortar and pestle with as purchased micron sized graphite (C) of different weight percentages (50–97.5%) and compacted into 11 mm diameter and 1–1.2 mm thick pellets. Samples are annealed at 600 °C and 1000 °C for 2 h under high vacuum (10^{-6} mbar) condition. Magnetization measurements were taken using vibrating sample magnetometer (Lakeshore 7410) system. MR measurements were done using a cryogen free superconducting magnet system (5TL-VRTB30, Janis Research Company, USA) by passing the current through the samples in both perpendicular (transverse) and parallel (longitudinal) directions to the applied magnetic field (up to 50 kOe) in the temperature range 4–300 K.

3. Results and discussion

The structural characterization and microstructure measurements have been discussed at length in our previous publication [19], which confirms that the as milled FeNi alloy powders are of average size ∼60 nm with a random shape, while electron diffraction pattern shows the presence of a two phase mixture, i.e., FeNi alloy and fcc-Ni. The longitudinal magnetoresistance (LMR) and transverse magnetoresistance (TMR) of all the samples up to the magnetic field of 50 kOe in parallel and perpendicular directions to the current flow respectively, have been carried out in the temperature range 300–4 K. MR is defined as $\Delta R/R = [R(H) - R(0)]/R(0)$; where $R(H)$ and $R(0)$ are the resistivity of the samples measured at an applied magnetic field H and without magnetic field. Fig. 1 shows MR as a function of applied field (H) at a temperature of 4 K. It is clear from Fig. 1(a) and (b), both LMR and TMR exhibit positive values though the magnitude of LMR is higher compared to TMR. All the composites of $(FN)_xC_{100-x}$ show similar variation of MR as a function of applied field. The LMR shows a linear behavior with H at higher applied fields but non-linearity could be noticed at lower fields. On the other hand, TMR shows linear behavior in the limited field range. There is no evidence of MR saturation up to a magnetic field of 50 kOe, indicating that the MR values could be much larger at high enough magnetic fields. Comparison of LMR and TMR data indicates that the magnitude of MR is direction dependent, which signals the presence of anisotropy. It is also to be noted from Fig. 1(a) and (b), that $(FN)_{15}C_{85}$ composition exhibits higher value of LMR, i.e., about 34% at 4 K compared to other compositions. The LMR values at 4 K (34%) are higher than that of 300 K (23%) under the

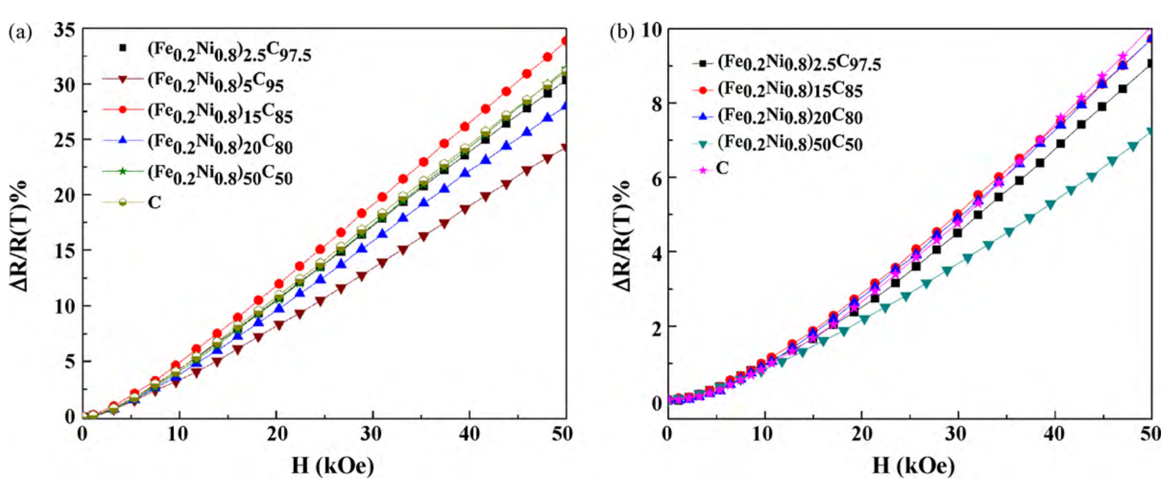

Fig. 1. (a) Longitudinal magnetoresistance as a function of applied magnetic field for $(Ni_{0.8}Fe_{0.2})_xC_{100-x}$ at 4 K and (b) transverse magnetoresistance as a function of applied magnetic field for $(Ni_{0.8}Fe_{0.2})_xC_{100-x}$ at 4 K.

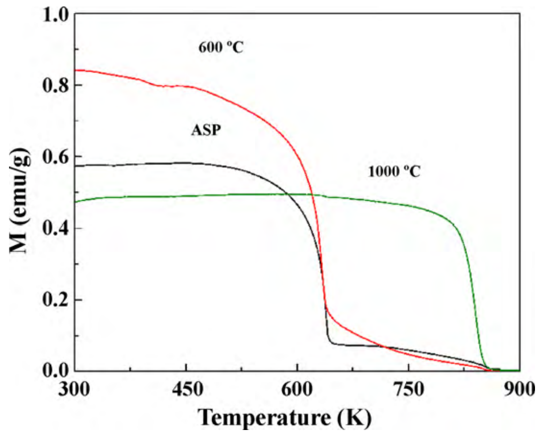

Fig. 2. Temperature variation of magnetization for as prepared (ASP) and annealed (600 °C, 1000 °C) samples of $(Ni_{0.8}Fe_{0.2})_5C_{95}$.

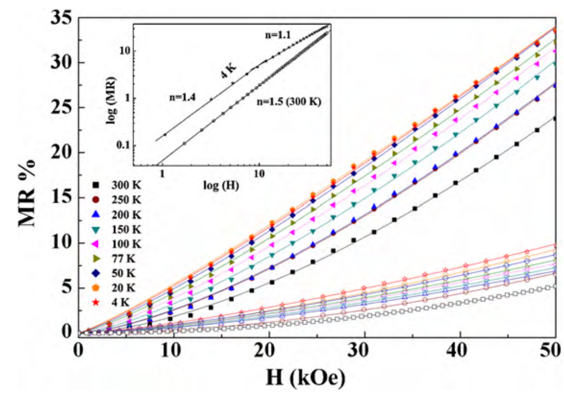

Fig. 4. Longitudinal and transverse magnetoresistance of $(Ni_{0.8}Fe_{0.2})_{15}C_{85}$ from 300 to 4 K. Closed symbols represent LMR and open symbols are for TMR. The solid lines represent fits to the data. Inset: log (*H*) vs. log (LMR) plot at 300 and 4 K.

same applied field. This is in agreement with the earlier reports [19]. Now a pertinent question that needs to be addressed is whether the magnetic properties of composites in anyway related to the positive MR values, their magnitude and linear field dependence? To seek an answer to this question we have carried out magnetic measurements as a function of temperature and field.

Fig. 2 shows the magnetization (*M*) as a function of temperature (*T*) in an applied magnetic field of 100 Oe for as prepared (ASP) and annealed samples of $(Ni_{0.8}Fe_{0.2})_5C_{95}$. At low applied fields, *M* increases for 600 °C annealed sample but decreases in the case of 1000 °C annealed sample. The as prepared and 600 °C annealed samples show double transition, one in between 600 and 650 K and the other at 850 K. These transitions are attributed to the presence of two FM phases, one being a major FN phase and other is elemental Ni. The existence of these two phases has been confirmed through the structural analysis and reported in earlier publication [19]. However, 1000 °C annealed sample shows a transition at 850 K in *M*(*T*) curve, indicating formation of homogeneous FeNi single phase. The magnetic isotherms at 300 K of as prepared and annealed samples of $(Ni_{0.8}Fe_{0.2})_5C_{95}$ as a function of applied magnetic field are shown in Fig. 3. As the annealing temperatures increases, the coercivity decreases from 73 to 7 Oe and saturation magnetization value increases which confirms that the annealed samples are magnetically softer. It is clearly seen that the transition observed at 650 K in *M*(*T*) curve disappears and a ferromagnetic to paramagnetic transition is shifted to 850 K. These measurements confirm that 1000 °C annealed sample is a single phase permalloy

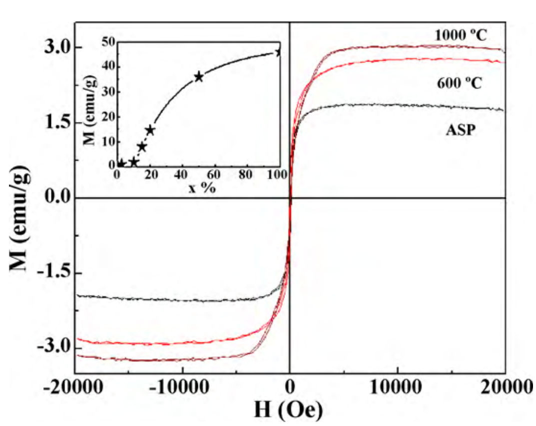

Fig. 3. Room temperature magnetization of as prepared (ASP) and annealed (600 °C, 1000 °C) samples of $(Ni_{0.8}Fe_{0.2})_5C_{95}$. Inset: saturation magnetization as a function of magnetic concentration (*x*).

with 850 K transition temperature and superior magnetic properties compared to as prepared samples. The reduction in strain of the ball milled FeNi particles on annealing at higher temperatures could also result in decrease of H_C. Inset of Fig. 3 shows the saturation magnetization as a function of magnetic concentration (*x*) for $(FN)_xC_{100-x}$. Magnetization of all the composites saturate below 5 kOe and the saturation magnetization (M_{sat}) values increase as the volume fraction of FN increased. On close observation of M_{sat} vs. FN concentration in graphite matrix, it is seen that the M_{sat} starts increasing rapidly above 15% and tends to saturate above 50%. This nature could be due to an increase in dipolar interactions above the percolative concentration. These observations suggest that the composites are ferromagnetic at lower temperatures, while graphite is non-magnetic but exhibits MR values of similar order and sign as that of composites. This observation suggests that the positive MR is most likely not associated with the magnetic properties of FeNi particles dispersed in the graphite matrix.

The magnetic field dependence of MR at 300 and 4 K appears to be somewhat different. In order to investigate this variation at different temperatures, the magnetoresistance isotherms were recorded for a typical composition $(FN)_{15}C_{85}$ in both the geometries (i.e., LMR and TMR) and are shown in Fig. 4. The MR vs. field curves show a systematic variation in the field dependence as the temperature is lowered. At 300 K, the LMR vs. *H* curves show linear field dependence at higher applied fields (limited field interval) and as the temperature is lowered, this linearity is extended down to lower field values. The range of linear region and the related exponent can be estimated by plotting a log(MR) – log(*H*) graph, which is shown in the inset of the figure at two extreme temperatures. The 300 K MR data shows an exponent close to 1.5 while 4 K MR exhibits two linear regions with exponent values 1.4 and 1.1. A similar behavior has been observed in the case of TMR as a function of applied field. Further the magnitude of MR increases, as the temperature is decreased which is similar to that observed in granular materials though the MR in the present case is positive. The high absolute electrical resistivity (ρ) values and negative temperature coefficient of resistivity (TCR) of all the composites suggest a semiconductor like behavior along with positive MR. Such high resistivity values could be due to the strong electronic disorder and explained on the basis of weak localization effects. In disordered systems the quantum interference effects (QIE) such as weak localization and electron–electron interactions can give rise to higher values of ρ and TCR. Our attempts to fit the data to the QIE theories did not however yield good fits. This is also in consistence with the magnetoresistance results [21,22], where it was argued that the weak localization effects might not be the primary mechanism causing negative TCR. Since the conventional theories proposed

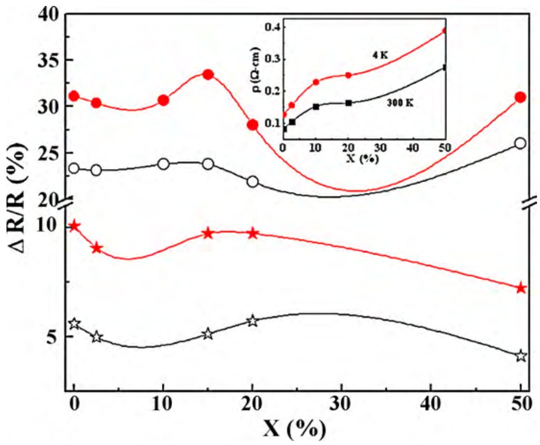

Fig. 5. Longitudinal and transverse magnetoresistance of $(Ni_{0.8}Fe_{0.2})_xC_{100-x}$ at 300 and 4 K. Circles are for LMR and Stars are for TMR. Open and closed symbols represent MR at 300 and 4 K respectively. Inset: change of resistivity as a function of magnetic concentration (x) at 4 and 300 K.

for metals and disordered alloys failed to explain the $\rho(T)$ behavior, alternative mechanisms to explain the non-metallic character have to be explored. Among the known mechanisms for positive MR, orbital effect is typically small, particularly for granular systems with small mean free path. Shrinkage of wave function due to applied field has been used to explain the positive MR in highly disordered semiconductors. When the electrical conduction is by either nearest neighbor hopping or variable range hopping, the positive MR can be described by quadratic field dependence below a certain critical field. However, the electrical resistivity data as a function of temperature does not follow variable range hopping (VRH) mechanism though the resistivity values are large. Therefore, we have attempted to identify the functional dependence of MR by fitting the data to the following equation

$$\frac{\Delta\rho}{\rho} = aH^n \quad (1)$$

where a and n are fitting parameters [19,23]. It can be seen from Fig. 4 that best fits were obtained for LMR with the exponent value $n \sim 1.6$–1.1 in the temperature 300–4 K. On the other hand, the exponent for TMR varies from ~2 to 1.3. This variation of field exponents cannot be explained using the existing theories on magnetic granular materials. Another interesting point is that $(FN)_{15}C_{85}$ composite exhibits large LMR values as compared to pure graphite, indicating that the magnetic component has some role in enhancing the MR value throughout the temperature range, though the major contribution comes from the graphite matrix owing to its semi-metallic character. Similarly all the composites show less TMR values compared to pure graphite. Pakhomov et al. have reported positive MR values at low and high temperature range while negative MR in the intermediate temperature range in submicron graphite powders [24]. They have attributed the positive MR to the shrinkage of the electron wave function and negative MR to interplay of the effects of level crossing and shifting in the magnetic field. However, such behavior has not been observed in the present investigations.

Fig. 5 shows the variation of LMR and TMR at 300 and 4 K as a function of magnetic particle concentration (x). In both the cases, $(FN)_{15}C_{85}$ exhibits the highest MR at a magnetic field of 50 kOe at 4 K. In the case of LMR, $(FN)_{15}C_{85}$ exhibits a comparable value (~34%) to that of pure graphite (~31%). Although we see some variation in MR values as a function of magnetic concentration, significant enhancement in MR has not been observed. Therefore we believe that magnetic particles are not solely responsible for large MR values though they play some role which gives rise to variations of MR as a function of x. These observations suggest that the semi-metallic nature of graphite particles play a significant role in this enhancement of MR values.

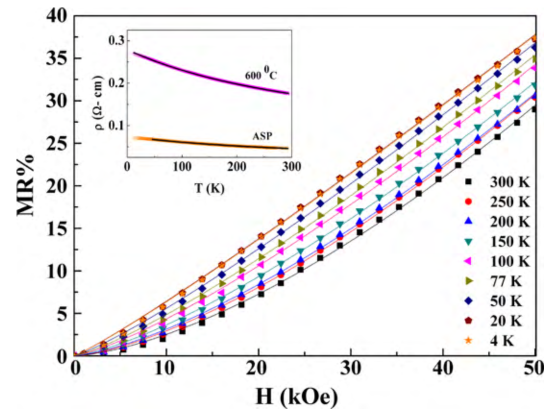

Fig. 6. Longitudinal magnetoresistance of 1000 °C annealed $(Ni_{0.8}Fe_{0.2})_5C_{95}$ from 300 to 4 K. Symbols represent the experimental data. The solid lines represent fits to Eq. (1). Inset: temperature variation of resistivity of as prepared (ASP) and 600 °C annealed $(FN)_5C_{95}$. The solid lines represent fits to Eq. (2).

In order to further investigate the origin of positive MR values, resistivity and MR measurements have been carried out on compacts of $(FN)_5C_{95}$ composite treated under different annealing temperatures 600 °C and 1000 °C. As shown in the inset of Fig. 6, the electrical resistivity (ρ) of as prepared and 600 °C samples show negative temperature coefficient of resistivity, which is indicative of non-metallic nature of the samples. The resistivity values of annealed sample are higher compared to as prepared sample. The resistivity data could be fitted to the fluctuation-induced tunneling (FIT) model, which is based on thermal fluctuations of electric potential on the edges of a tunneling gap. This model predicts the temperature dependence of resistivity as

$$R = R_0 \exp\left[\frac{T_1}{T_0 + T}\right] \quad (2)$$

where R_0 is a parameter which depends weakly on temperature, and T_1 and T_0 are characteristic temperatures [19,25]. The LMR of 1000 °C annealed $(FN)_5C_{95}$ sample (see Fig. 6) shows positive MR values throughout the temperature range, while the as prepared and 600 °C annealed $(FN)_5C_{95}$ samples show similar behavior with lower MR values. From Fig. 7, it is clear that as the annealing temperature increases, MR is also increasing. It is interesting to point out here that enhanced magnetization (Fig. 3) and resistivity (Fig. 6) values in annealed samples throw more challenges in

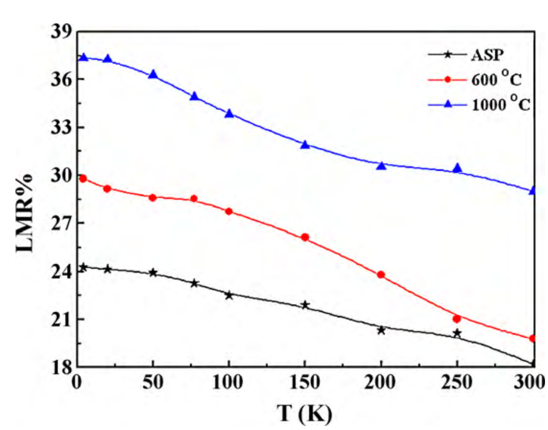

Fig. 7. Change of longitudinal magnetoresistance as a function of temperature (300–4 K) for as prepared (ASP) and annealed (600 °C, 1000 °C) samples of $(Ni_{0.8}Fe_{0.2})_5C_{95}$.

identifying the origin of the enhanced MR. From composition variation as well as annealing temperature effects on magnetization and MR results, we see no systematic correlation between the magnetic and MR properties. However, some similarities could be seen between the resistivity and MR behavior, which suggest that the dominant contribution comes from the matrix, i.e., graphite semi-metallic nature rather than the magnetic particles. We conclude that the large positive MR values at low temperatures are probably due to the semi-metallic nature of the graphite matrix and the variations observed on magnetic particle substitution could be due to the small negative magnetoresistance due to the presence of magnetic constituent in the matrix.

4. Conclusions

Magnetic and electrical transport properties of $(Ni_{0.8}Fe_{0.2})_x C_{100-x}$ granular composites have been investigated in the temperature range 4–300 K. All the samples of present study exhibit positive magnetoresistance values at all fields and temperatures. A maximum of ~35% MR in longitudinal geometry is observed at 4.2 K which decreases with increasing temperature. Although magnetic and MR behavior show some similarity, we suggest the dominant positive MR stems from the semi-metallic graphite matrix rather than the magnetic components.

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