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Dedicated to Professor Dr. Sorin Dan Anghel on His 65th Anniversary

EFFECT OF STARTING POWDER PREMIXING ON THE INTERPHASE EXCHANGE COUPLING IN $Nd_2Fe_{14}B$ + 10 WT % Fe NANOCOMPOSITES OBTAINED TROUGH MECHANICAL MILLING

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ABSTRACT. In the frame of optimizing the potential, of had /soft nanocomposites for high performance applications, we report on the effect of starting powder premixing on the structure, microstructure and exchange coupling in hard/soft magnetic phases. $Nd_2Fe_{14}B$ powder was first mixed with Fe powder using two different means: by hand or by using a Turbula Mixer. Moreover, in the hand mixed powders the Fe particle size was changed from 100 to 1 µm, while the samples mixed using the Turbula Mixer contained only Fe particles of around 1 µm in size. The mixed powders were subsequently milled for 6 hours in a planetary ball mill; the calculated impact energy was 77 mJ/impact and 10 kJ/g for the entire duration of process. Good exchange coupling was obtained in all three cases. The samples prepared with Fe < 1 µm particles yielding slightly better results due to better dispersion of the two phases in the final nanocomposite material. The highest energy product was achieved for the sample premixed with the Turbula Mixer ($(BH)_{max}$=125 kJ/m^3) after being annealed at 800 °C for 1.5 min.

Keywords: *spring magnet, milling, short time annealing, mixing method*

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INTRODUCTION

Permanent magnets are crucial components in many of today's devices, finding their way in a wide range of either ubiquitous or high-tech applications, from windscreen wipers and smart phones to electric cars and wind turbines (Nd-Fe-B magnets have a high end market share of over 50%) [1-3]. Due to the high reliance on rare-earth magnets, pricing issues and the availability of raw materials, several research avenues have been opened to address the problem [4]: the development of new magnetic materials, the investigation of older compounds with potentially high energy products $(BH)_{max}$, the creation of soft/hard magnetic nanocomposites (spring magnets) [5] with a predicted energy product of 1 MJ/m^3 [6], Recycling [1] etc. Soft/hard magnetic nanocomposites are comprised of a fine mixture of exchange coupled hard and soft magnetic phases, ensuring high coercivity, high remanence, and potentially very competitive magnets when comparing the theoretical energy product with current commercial products. The $Nd_2Fe_{14}B$/α-Fe spring magnet is interesting not only because of its possible applications, but also from a fundamental research point of view [1-3]. The advantages of spring magnets are numerous: increased thermal stability [7-9], high corrosion resistance [10] and a very high potential energy product [6], but the challenges involved in obtaining such materials are also significant. In order to ensure a good degree of interphase exchange coupling the crystallite size of the soft magnetic phase cannot exceed twice the domain wall thickness of the hard magnetic phase (which presents difficulties with annealing processes), moreover the two magnetic phases must be homogeneously interspersed. The structure and magnetic properties of 6 h mechanically milled (MM) nanocomposites $Nd_2Fe_{14}B$/α-Fe were previously studied [11]. After milling, the samples showed poor crystallinity and high defect density. It was shown that the crystallinity of the hard magnetic phase can be restored through short time heat treatment at high temperature, thus limiting the growth of the soft phase crystallites. Therefore, in our current work we have chosen to study the effect of the soft-hard inter-dispersion by mixing the starting powders ($Nd_2Fe_{14}B$ and α-Fe powder) in several ways, before undergoing the milling and short time annealing procedures, in order to gain a better understanding of the entire synthesis process.

EXPERIMENTAL DETAILS

The $Nd_2Fe_{14}B$ ingots were prepared by first arc-melting the appropriate amount of $Fe_{14}B$ alloy and second a melting along with the stoichiometric amount of Nd in an induction furnace. The resulting ingots were then annealed at 950 °C for 72 h in order to stabilize the structure and ensure the homogeneity of the samples. The

$Nd_2Fe_{14}B$ Ingots were crushed and sieved through a sieve with an opening of 500 µm and the resulting powder was mixed with 10 wt% Fe powder. Three powder mixtures were created by varying the type of Fe powder, and mixing method (Table 1).

Table 1. Composition and premixing method for each of the three $Nd_2Fe_{14}B$ + 10 wt% Fe starting powders

$Nd_2Fe_{14}B$ powder 90 wt%	Fe powder 10 wt%	Mixing Method
Particle size < 500 µm	Particle size < 100 µm	By hand 5 min
Particle size < 500 µm	Particle size < 1 µm	By hand 5 min
Particle size < 500 µm	Particle size < 1 µm	Turbula mixer 15 min

The first mixture was made using Fe < 100 µm and was mixed by hand (HM) for 5 minutes using a spatula. The second mixture was made by using Fe < 1 µm and was also HM for 5 minutes. The last mixture was made using Fe < 1 µm and was mixed for 15 minutes using a Turbula Mixer (TM). Each $Nd_2Fe_{14}B$ + 10 wt% Fe powder mixture was then milled in a planetary ball mill (Frisch Pulverisete 4) for 6 h under Ar gas. The milling vials (80 ml) and balls (15 mm in diameter) were made of 440 C hardened steel. The ratio between the rotation speed of the disc and the relative rotation speed of the vials was Ω/ω = 333/900 rpm with a ball-to-powder weight ratio of 10:1. The milled samples were then annealed at 700, 750 and 800 °C for 1.5 min and rapidly cooled by immersing in water. The energies involved in the milling process were estimated trough computer simulation using the model proposed by M. Abdellaoui and E. Gaffet [12]. The calculations yielded the following values: Shock energy 77 mJ/impact, Friction 10 mJ/impact, Total Shock energy of 26 kJ/g. The effective impact frequency (the frequency with which a ball hits the same powder particle) was also calculated as 0.14 Hz [13]. The structure and microstructure of the annealed samples was investigated by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with a Cu source and Bragg Brentano focusing geometry. The mean crystallite sizes were evaluated from Scanning Electron Microscopy (SEM) images and trough the Scherrer [14] method from XRD. The full width at half maximum (FWHM) of α-Fe (2θ = 82.3°) and $Nd_2Fe_{14}B$ (2θ = 37.3°) peaks was determined by fitting the peaks with the sum of two Pseudo-Voight functions of the same shape and an intensity ratio of 0.5 (corresponding to the Cu-Kα1 and Kα2 components of the X-ray radiation). Because the evaluations were made on annealed samples, the influence of internal stress on the FWHM was neglected. For magnetic measurements, the powder samples were blocked in epoxy resin. The demagnetization curves were recorded at 300 K using the extraction method in applied fields of ±10 T. Considering isolated spherical magnetic particles we used a demagnetization factor of 1/3 for the magnetic data and for the calculation of the internal field, H_{int}.

RESULTS AND DISCUSSIONS

The XRD patterns for all milled and annealed samples, Figure 1, show an increase in the crystallinity of both the $Nd_2Fe_{14}B$ and α-Fe phases as the annealing temperature increases from 700 to 800 °C. No significant differences could be observed between the samples annealed at the same temperature.

The average crystallite sizes for the soft magnetic phase (Figure 2) present the same behavior for all three starting powder types, the Fe < 1 µm starting powder yielding the same values (within the experimental error) as the Fe < 100 µm starting powder.

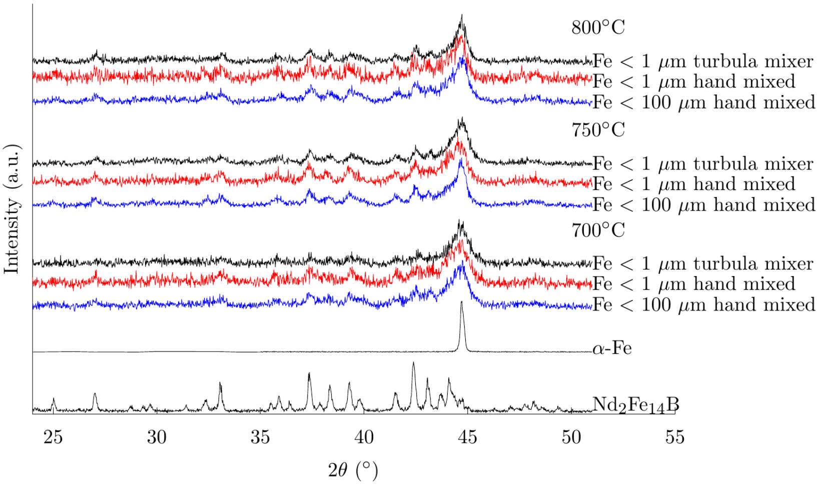


Figure 1. Normalized XRD patterns for the 6 h MM and annealed for 1.5 min at 700, 750 and 800 °C $Nd_2Fe_{14}B$ + 10 wt% α-Fe nanocomposite samples obtained using the 3 different starting powders

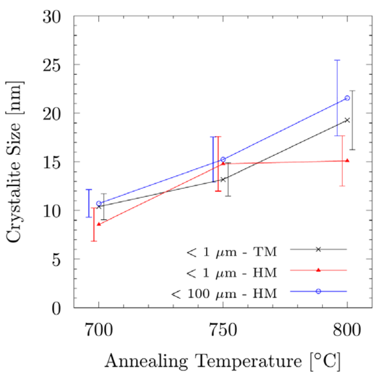
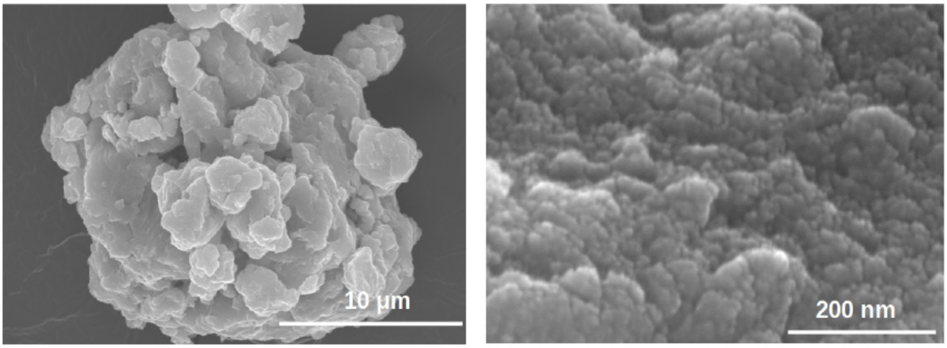
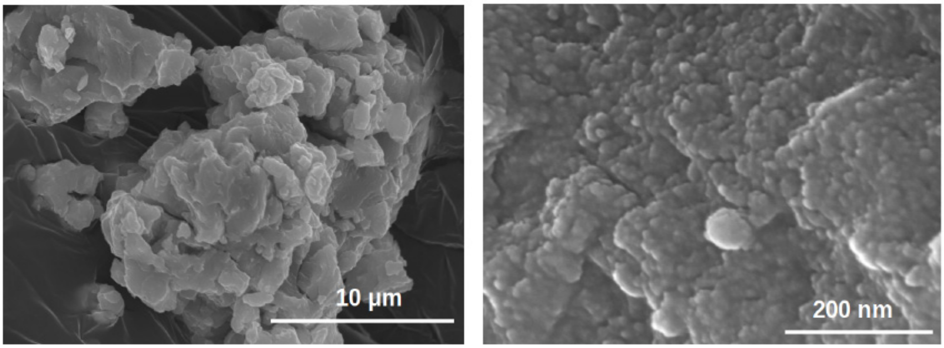


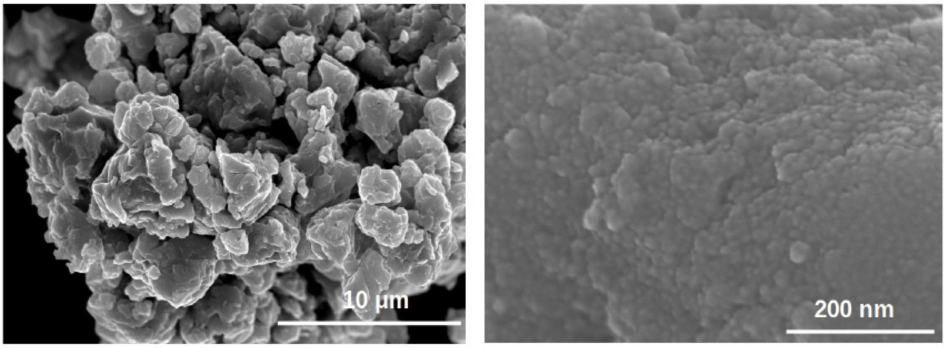
Figure 2. Average crystallite sizes corresponding to soft α–Fe phase for the 6 h MM and annealed for 1.5 min at 700, 750 and 800 °C $Nd_2Fe_{14}B$ + 10 wt% α-Fe nanocomposite samples obtained using the 3 different starting powders



(a) Fe < 1 μm - Mixed using Turbula Mixer



(b) Fe < 1 μm - Mixed by hand



(c) Fe < 100 μm - Mixed by hand

Figure 3. SEM images of 6 h MM $Nd_2Fe_{14}B$ + 10 wt% Fe

SEM images of the three different sample sets were taken in Figure 3. At a scale of 10 µm we clearly see that the powder particles are formed of agglomerations of nano-crystallites, while the images taken at a higher magnification (200 nm) support the values for the average grain sizes assessed trough XRD (Figure 2).

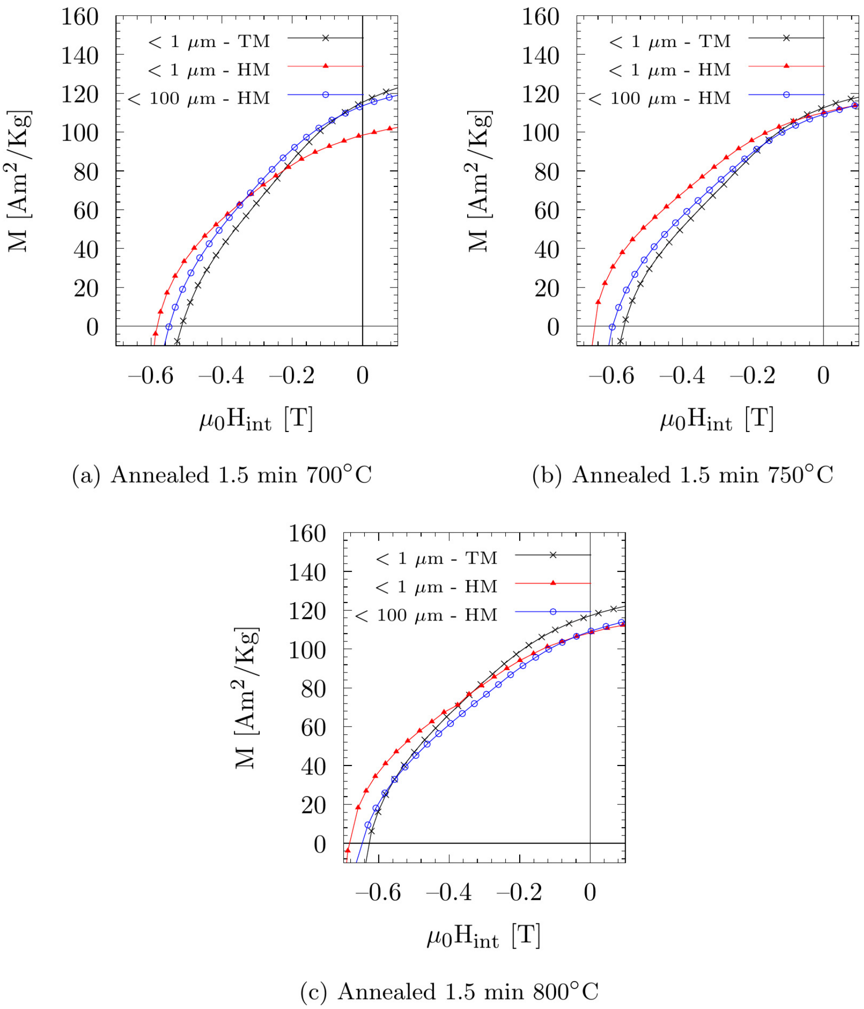
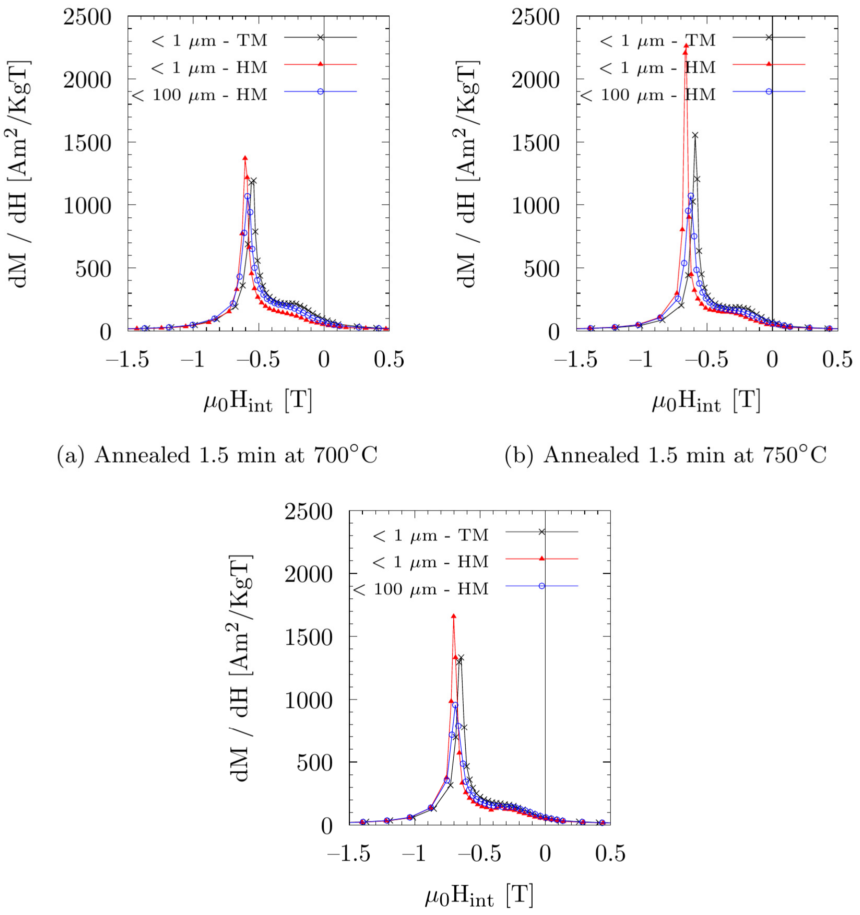


Figure 4. Demagnetization curves at 300 K for the 6 h MM and subsequently annealed $Nd_2Fe_{14}B$+10 wt% Fe nanocomposite powders obtained from the 3 different starting powder mixtures

From the demagnetization curves (Figure 4) we can see that the magnetic properties of all samples improve with increasing annealing temperature: the coercivity, the remanence and the squareness of the demagnetization curves increase. The samples annealed for 1.5 min at 800 °C (Figure 4c) presenting significant improvements over the ones annealed for the same time at 700 °C (Figure 4a). Of these we note the very smooth curve of the sample which was premixed using the Turbula mixer which is indicative of good exchange coupling.



(a) Annealed 1.5 min at 700°C (b) Annealed 1.5 min at 750°C

(c) Annealed 1.5 min at 800°C

Figure 5. Derivative of the magnetization at 300 K as a function of the internal field for the 6 h MM and subsequently annealed $Nd_2Fe_{14}B$ + 10 wt% Fe nanocomposite powders obtained from the 3 different starting powder mixtures

The quality of the magnetic interphase exchange coupling was further evaluated by *dM/dH* vs *H* plots (Figure 5) where the peaks at high fields are indicative of good exchange coupling between the two phases, while the peaks at low values of H denote poor exchange coupling of soft phase with high coercivity hard magnetic phase. The samples annealed for 1.5 min at 700 °C (Figure 5a) present a similar behavior, with a large peak at high field and a very small one at low values of H. As the annealing temperature is increased to 750 °C (Figure 5b) the samples produced with Fe < 1 µm show a much higher peak at high fields than the sample produces with the starting powder containing larger Fe < 100 µm. All other things being the same, this implies that the smaller grains allow for a better dispersal of the Fe particles which in turn lead to improved magnetic interphase exchange coupling. At the highest annealing temperature (Figure 5c) the samples produced with Fe < 1 µm still present the higher peaks at high field. The samples which were mixed by hand show a very small peak at low field while the ones mixed with a Turbula mixer present a smoother transition. Continuing our previous reasoning we must conclude that the slight improvement in exchange coupling is due to the very good dispersal of α-Fe in the $Nd_2Fe_{14}B$ + α-Fe starting powder by Turbula mixing.

In the case of the coercive field, Figure 6a, we can see that it increases slightly with annealing temperature, for all samples due to the increase in the crystallinity of the hard magnetic phase. Furthermore, across all temperatures, the hand mixed samples present higher values for the coercive field. This could be viewed as an indirect indicator for the efficiency of the magnetic interphase exchange coupling due to the fact that we generally see a drop in H_c and an increasing of M_r when coupling takes place. Furthermore this behavior correlates with the slightly higher remanence exhibited by the samples mixed with a Turbula mixer, Figure 6b.

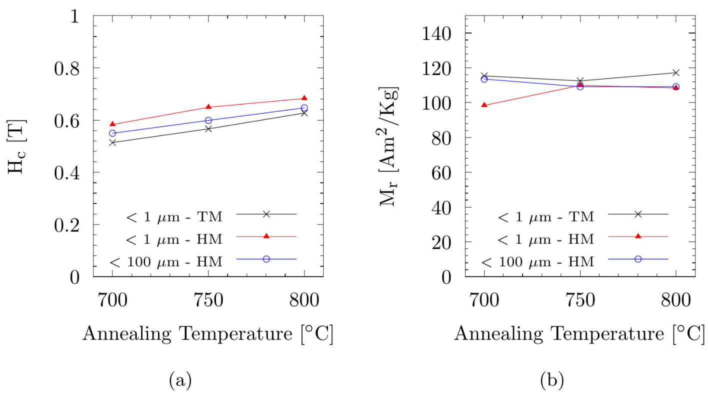


Figure 6. Coercive field (a) and Remanence (b) for the 6 h MM and subsequently annealed $Nd_2Fe_{14}B$ + 10 wt% Fe nanocomposite powders obtained from the 3 different starting powder mixtures

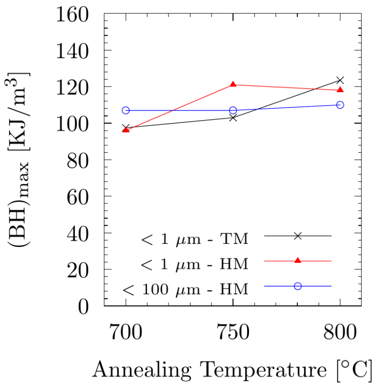


Figure 7. Energy product $(BH)_{max}$ for the 6 h MM and subsequently annealed $Nd_2Fe_{14}B$ + 10 wt% Fe nanocomposite powders produces from the 3 different starting powder mixtures

The energy product $(BH)_{max}$ was calculated for the 6 h MM and annealed samples (Figure 7). The samples prepared with Fe < 1 µm show an increase in the energy product with the increase in annealing temperature, while for the samples prepared with the powder mixture containing larger Fe particles the energy product remains relatively constant. The highest energy value 125 kJ/m^3 was recorded for the samples prepared using the Turbula mixer.

CONCLUSIONS

In summary the effect of starting powder premixing on the interphase exchange coupling in $Nd_2Fe_{14}B$ + 10 wt% α-Fe nanocomposites was studied by varying the size of the initial Fe particles (1 or 100 µm) and by varying the mixing method (by hand or using a Turbula mixer). After annealing at 700, 750 and 800 °C small improvements in the demagnetization curves were observed for the samples made using the smaller Fe particles as they can disperse better in the nanocomposite. Moreover further improvement was obtained when using the Turbula mixer denoted by the smoothness of the demagnetization curve and by the correlated variation in H_c and M_r.

To conclude, increasing the homogeneity of the starting powder slightly increases magnetic performance in $Nd_2Fe_{14}B$ + 10 wt% α-Fe obtained by mechanical milling. The highest energy product of 125 kJ/m^3 being obtained for the sample premixed using a Turbula mixer.

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