The Pulse-Thermal Processing of NdFeB-Based Nanocomposite Magnets

Z.Q. Jin, V.M. Chakka, Z.L. Wang, J.P. Liu, P. Kadolkar, and R.D. Ott

Pulse-thermal processing (PTP) based on high-density plasma arc lamp technology has been utilized to crystallize melt-spun NdFeB-based amorphous ribbons to form magnetic nanocomposites consisting of $Nd_2Fe_{14}B$ and α-Fe phases. After applying suitable pulses, the NdFeB-based ribbons were developed with hard magnetic properties. The highest coercivity can be obtained for ribbons with a thickness of 40 μm after PTP treatments consisting of a 400 A pulse for 0.25 s for ten times. The correlation between PTP parameters and magnetic properties indicates that PTP is an effective approach to control the structure and properties of nanostructured magnetic materials. Transmission-electron microscopy analysis revealed that the observed decoupling between the hard and the soft phases is related to large grain size in the samples, which is in turn related to different heating conditions in different regions of samples.

INTRODUCTION

Nanocrystalline materials possess physical and chemical properties quite different from those of conventionally coarse-grained materials. As a subset of nanomaterials, nanocomposite permanent magnets have been a hotspot in a long-term search for high-performance magnets. Coehoorn et al.[1] in 1989 observed magnetic exchange interaction at nanoscale between a magnetically hard phase with high anisotropy and a magnetically soft phase with high magnetization, which may lead to very high magnetic energy products in the exchange-coupled nanocomposite magnets. Numerous investigations have been made since then. It has been revealed that a deliberate control of nanostructure is the preliminary assurance of improved magnetic properties in the nanocomposites.[2–8] The nanostructured composites can be obtained by using techniques including melt spinning, mechanical milling, sputtering, atomization, and chemical synthesis. With most of these techniques, subsequent heat treatments are necessary to control phase structure and morphology.

Rapid thermal processing (RTP) techniques[9–13] have been applied to process nanocomposite magnets. High heating rates up to several hundreds of degrees per second, the utilization of direct current, or extremely short compaction durations of microseconds distinguish them from conventional processing technologies that lead to excessive grain growth. High coercivity values have been achieved in RTP-processed nanostructured NdFeB,[9] SmCo,[10] and FePt thin films.[14] A recent investigation revealed that heating time as short as 1 s results in a high degree of magnetic hardening and complete crystallization in amorphous NdFeB ribbons.[15] This interesting finding leads to a key question: how fast can magnetic hardening be realized in a given magnetic material? This paper reports preliminary results achieved using pulse-thermal processing (PTP) of an NdFeB-based nanocomposite magnet. The PTP technique has the capability of reaching extremely high heating rates (up to 600,000°C/s) by utilizing high-density plasma arc lamp technology.[16,17] The high heating rate combined with short dwell time at maximum temperature ensures a controlled diffusion on the nanoscale in processed materials.

See the sidebar for experimental procedures.

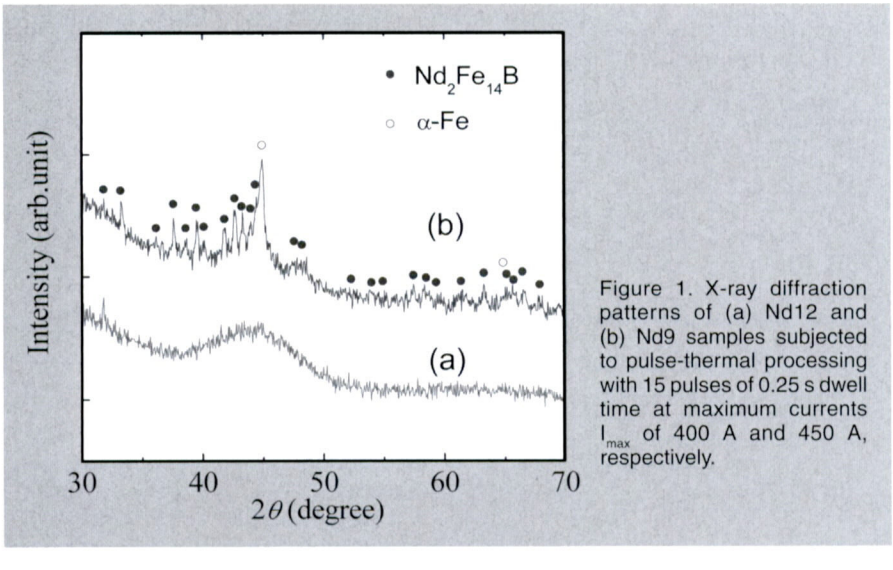

Figure 1. X-ray diffraction patterns of (a) Nd12 and (b) Nd9 samples subjected to pulse-thermal processing with 15 pulses of 0.25 s dwell time at maximum currents I_{max} of 400 A and 450 A, respectively.

RESULTS AND DISCUSSION

Phase Structure and Magnetic Properties of the PTP Samples

The initial objective of this work is to verify the feasibility of the PTP technique for processing of magnetic nanocomposites, thus the investigation was first done on the crystallization of amorphous ribbons by changing the incident power and exposure time. The thermophysical properties of the samples, including emissivity, specific heat, density, and thermal conductivity

all combine to determine the heating temperature and are difficult to measure. Therefore, the pulse power output was used to characterize the heating conditions and control the crystallization of the amorphous phase. Figure 1 shows the x-ray diffraction (XRD) profiles for Nd9 and Nd12 samples exposed to multi-pulses with maximum currents I_{max} of 450 A and 400 A, respectively. Before the PTP treatment, all of the samples were amorphous. After the PTP treatment, the thick Nd12 ribbons show no significant crystallization due to their large thickness (above 200 μm) and the low heating power output of I_{max} = 400 A. The amorphous structure of Nd12 ribbons shows no magnetic coercivity for power output up to 550 A as evident from the magnetic measurements. Thin Nd9 ribbons (around 40 μm thick) show a crystallized nanocomposite structure containing a hard magnetic tetragonal $Nd_2Fe_{14}B$ phase and soft magnetic α-Fe phase. The intensity distribution of the $Nd_2Fe_{14}B$ peaks indicates no texture in the samples. Higher-power pulses resulted in overheating and even melting, which led to significant grain growth and subsequent magnetic softening.

Magnetic measurement was then carried out to analyze the phase structure and magnetic property evolution. The measurement showed that the as-spun ribbons of amorphous structure are magnetically isotropic with nearly zero coercivity. After heat treatment, coercivity was developed. Figures 2 and 3 present the hysteresis loops obtained for Nd12 and Nd9 samples treated with different PTP variables. Because of the extremely short processing time of PTP techniques compared to furnace processing, the annealing time (i.e., the dwell time and pulse number) will be a key parameter for controlling the magnetic properties. It can be seen that for Nd12 samples, the starting ribbon materials are completely soft with undeveloped coercivity (<3 Oe). After the PTP processing, most samples were still soft while only those processed with a pulse current I_{max} above 550 A and a pulse dwell time t of 0.1 s had been developed with hard magnetic properties although their coercivity values are quite modest (200 Oe for I = 525 A and 500 Oe for I = 550 A). Prolonged dwell times do not promote the development of magnetic hardening for the pulse current below 500 A. It was confirmed that a pulse current greater than 550 A is necessary for inducing crystallization of the Nd12 sample while a 600 A pulse current has resulted in the burning trace and reduction of magnetic properties, revealing a very narrow PTP window for the optimization of magnetic properties. This narrow processing window should be related to the large thickness of the ribbons due to the low thermal conduction performance of materials relative to the short pulse process time. With reduced ribbon thickness, the extension of the optimal processing window should be expected, as evidenced by the result for Nd9 samples of around 40 μm thick. The half hysteresis loops (Figure 3) show that when the current is above 550 A, the samples (B1 and B2), which had a burned appearance, show a very low coercivity, apparently due to grain coarsening. A current below 525 A is necessary for achieving high coercivity. The highest coercivity of 5.2 kOe was obtained for the sample processed with condition B8, where a pulse current of 400 A was applied with a short pulse duration (10 pulses of 0.25 s). It is noted that most PTP-processed Nd9 samples have steps on the hysteresis loops. This indicates that the exchange coupling

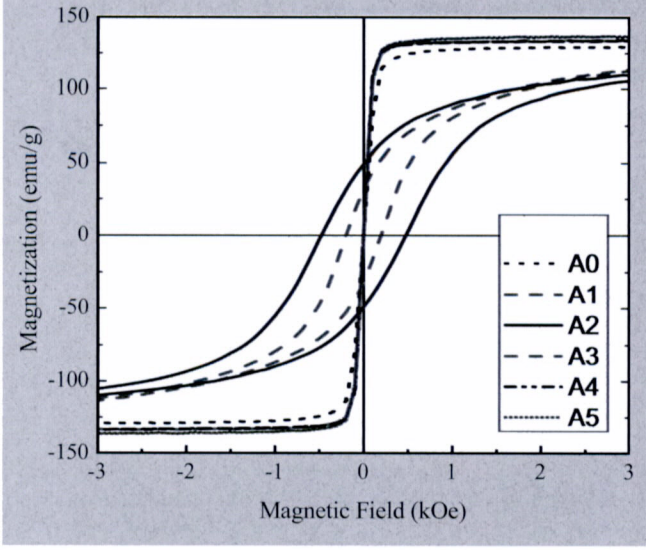

Figure 2. Hysteresis loops for Nd12 samples with different PTP variables. (A0) starting amorphous ribbons; (A1) five pulse currents with I_{max} of 600 A and 0.1 s dwell time for each pulse; (A2) five pulses, 550 A, 0.1 s; (A3) five pulses, 525 A, 0.1 s; (A4) 15 pulses, 450 A, 0.25 s; (A5) 15 pulses, 400 A, 0.25 s.

EXPERIMENTAL PROCEDURES

The starting materials used for this investigation were melt-spun amorphous ribbons 2–4 mm in width. A thin ribbon sample (40 μm in thickness, noted as Nd9) had a composition of $Nd_2Fe_{14}B$ as the primary phase with an additional 20 vol.% α-Fe. A thick ribbon sample (200 μm in thickness, noted as Nd12) had a stoichiometric composition close to $Nd_2Fe_{14}B$. The pulse-thermal processing was carried out at Oak Ridge National Laboratory using a high-density plasma arc lamp to heat ribbon samples in argon within several short pulses with controlled power output and dwell time. The utilization of the plasma arc lamp generates a power density of ≤3.5 kW/cm² over an area of 1 × 10 cm². Since single-pulse heating is not enough for the crystallization of amorphous samples, a multi-pulse heating mode was used with a preheating with a 50 A pulse current for 3 s and followed by multi-pulse heating with pulse currents of 400 A, 450 A, 500 A, 525 A, 550 A, and a maximum power output of 600 A. The exposure time of each pulse is 0.25 s for a current of 400 A and 450 A (five, ten, and 15 pulses), and 0.1 s for currents above 525 A (five pulses), respectively.

A Siemens D500 powder x-ray diffraction (Philip-Cu K_α radiation) and a JEOL-2010 transmission-electron microscope were used to examine the structural and grain morphologies. The magnetic properties of crystallized samples were measured using an alternating gradient magnetometer at a low applied field of 1.4 T. After several measurements, it was found that the ribbons prepared in the same melt-spinning process with the same composition exhibited minor differences in their magnetic properties, which may be due to non-uniformity in their phase structure and composition. Therefore, to ensure the reproducibility of the measurements, each measurement was based on an average of several samples.

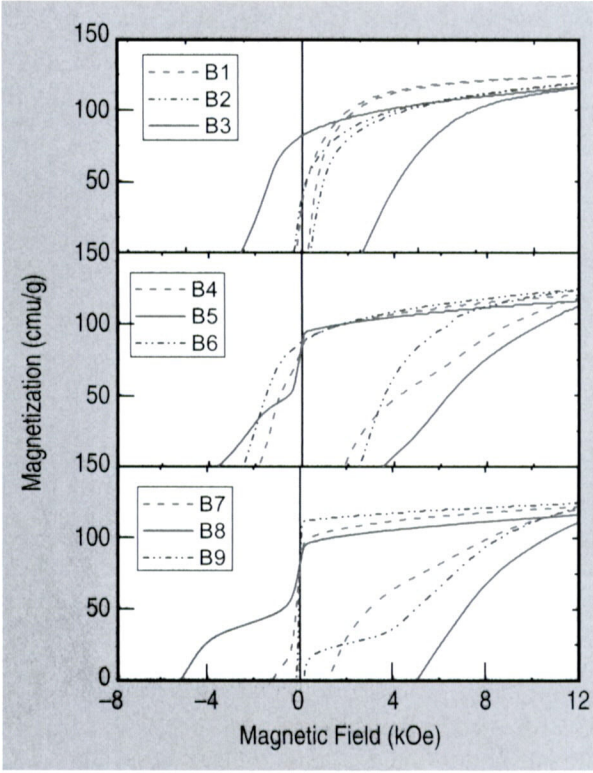

Figure 3. Half-hysteresis loops for Nd9 samples with different PTP variables. (B1, B2, B3) are five pulse currents of 0.1 s dwell time for each pulse and with I_{max} = 600 A, 550 A, and 525 A, respectively; (B4, B5, B6) are five pulses, ten pulses, and 15 pulses, respectively, of 0.25 s and with I_{max} of 450 A; (B7) five pulses, 400 A, 0.1 s; (B8, B9) ten and 15 pulses, respectively, with 400 A and 0.25 s.

between the hard and soft phases is not strong, which may be due to the large grain size of iron or to the non-uniformity in microstructure along the cross section, which is very sensitive to the thermal conductivity of the materials during the thermal processing. This study also revealed that five heating pulses with dwell times of 0.1 s are not enough to achieve optimal magnetic properties at this current (B7). The coercivity is only one fourth of the highest value.

With the comparison of magnetic properties of PTP-processed thick and thin ribbons, it is believed that during the PTP treatment extremely high energy with a very short dwell time was employed initially on the ribbon surface to produce a large thermal gradient within the samples. Subsequent annealing was realized by thermal conduction from the surface to the inside of the ribbons. The huge vertical and lateral temperature gradient within the ribbon leads to the non-uniformity of microstructure where crystallized and amorphous regions coexist, resulting in the occurrence of steps on the hysteresis loops. The large temperature gradient is related to thermal conductivity and capacity of the materials. At high current, local elevated temperature incurred at the surface might be above the melting point, resulting in the occurrence of a burning trace. At low current, the thermal conductivity may not be enough to fully crystallize the amorphous regions within the ribbons, giving rise to the decoupling between the hard and soft phases.

Morphology of the PTP Samples

Figure 4 shows transmission-electron microscopy (TEM) images of PTP-processed Nd9 samples corresponding to an I_{max} of 525 A with five pulses of 0.1s, an I_{max} of 450 A with 15 pulses of 0.25 s, and an I_{max} of 400 A with ten pulses of 0.25s. It is interesting to note that the PTP-processed samples apparently have very large grain sizes (100–200 nm), significantly larger than those (30–90 nm) of conventional furnace-annealed samples and those (20–50 nm) of RTP samples.[15] It seems that a high-pulse-current-processed sample has a more clear grain interface than low-current-processed samples. The latter has a non-uniform size distribution, which may account for the large step on the loop although relatively large coercivity was obtained. Most of the grains do not show spherical morphology but an irregular and even elongated shape of 200 nm grain size. This is different from conventionally furnace-treated and rapidly thermal-processed samples where much uniform morphology was observed. High-resolution TEM revealed the existence of remaining amorphous phase as shown in Figure 5, even in the case of 450 A. This indicates that the rapid crystallization and grain growth are very localized, possibly due to the

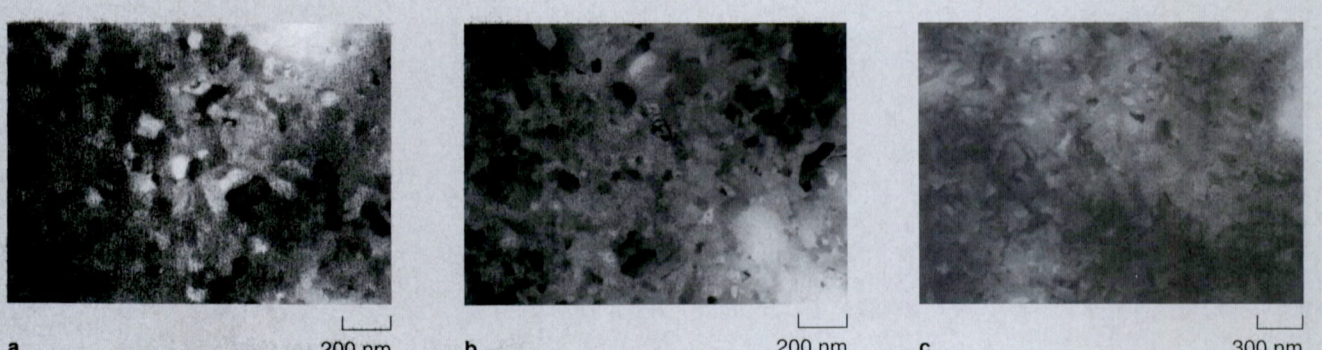

Figure 4. Transmission-electron microscopy images of Nd9 samples subjected to PTP with different parameters. (a) I_{max} of 525 A with five pulses of 0.1 s, (b) I_{max} of 450 A with 15 pulses of 0.25 s, and (c) I_{max} of 400 A with ten pulses of 0.25s.

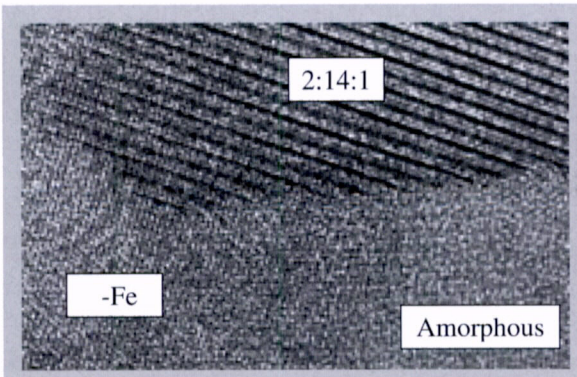

Figure 5. A high-resolution TEM image of Nd9 samples subjected to PTP with 15 pulses of 0.25 s dwell time at I_{max} = 450 A.

extremely high incident energy, while no structural defect was observed in crystallized $Nd_2Fe_{14}B$ grains. The existence of large soft grains and amorphous material eases domain wall movement and nucleation of reversal domains, leading to reduced magnetic hardening. When the dimension of the soft magnetic region is larger than the required exchange length (~10 nm), significant decoupling will occur as revealed in Figure 3. This shows a fine tuning of PTP parameters is necessary to excavate the potential in processing nanocomposite magnets.

CONCLUSIONS

This study found that an annealing time as short as 0.5 s initiates a crystallization transition from an amorphous phase to magnetic nanocomposite, while prolonged processing is required for optimization of magnetic hardening in the ribbons. The power output required for thin ribbons is apparently smaller than that for thick ribbons. At low power output, the optimization of experimental parameters is more controllable. Crystallized samples show elongated grain morphology with a mean grain size above 200 nm. Although more work needs to be done in the optimization of processing parameters, the correlation between the PTP parameters and the magnetic properties shows that PTP is effective for investigating the rapid evolution of microstructure and properties of nanostructured magnetic materials.

ACKNOWLEDGEMENT

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