3D printing of anisotropic Sm–Fe–N nylon bonded permanent magnets

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Abstract
Fabricating a bonded magnet with a near-net shape in suitable thermoplastic polymer binders is of paramount importance in the development of cost-effective energy technologies. In this work, anisotropic Sm2Fe17N3 (Sm–Fe–N) bonded magnets are additively printed using SmFeN anisotropic magnetic particles in polyamide-12 (PA12). The anisotropic SmFeN bonded magnets are fabricated by Big Area Additive Manufacturing followed by post-printing alignment in a magnetic field. Optimal post-alignment results in an enhanced remanence of \( \sim 0.68 \) T in PA12 reflected in a parallel-oriented (aligned) measured direction. The maximum energy product achieved for the additively printed anisotropic bonded magnet of Sm–Fe–N in PA12 polymer is 78.8 KJ m\(^{-3}\). Our results show advanced processing flexibility with 3D printing of the development of SmFeN nylon bonded magnets designed for applications with no critical rare earth magnets.

KEYWORDS
additive manufacturing or 3D printing, magnetic properties, mechanical properties, SmFeN nylon bonded permanent magnets

JEL CLASSIFICATION
Materials science

1 | INTRODUCTION

High-performance hard magnets based on Nd–Dy–Fe–B are extensively used in devices and systems for different applications including hybrid electric vehicles.\(^1\)–\(^4\) Nd and Dy are critical for high energy density and efficiency at high operating temperatures but they are also vulnerable to potential supply chain disruption. Hence, the increased demand for high-performance sintered magnets has stimulated intense research in developing alternatives to Nd–Dy–Fe–B magnets. Sm2Fe17N3 (Sm–Fe–N) compound is known to have a high Curie temperature, high saturation magnetization, and a large anisotropy field\(^5\) and thereby seems suitable for advanced technological applications. However, Sm2Fe17N3 alloy powder cannot be sintered since it is not stable at high temperatures but decomposes into \( \alpha \)-Fe and Sm–N phases above 873 K.\(^6\) To
achieve densification and avoid decomposition, various approaches have been adopted including shock compaction,\textsuperscript{7,8} hot-pressing,\textsuperscript{9} and compression shearing methods.\textsuperscript{10–12}

Manufacturing of bonded magnets has greater flexibility over both sintered and hot deformation techniques. Compression and injection molding are the benchmark techniques for fabricating bonded magnets. Both methods enable manufacturing of complex and near net shape geometries, but require specific tooling for each design which increases the product costs. In this context, additive manufacturing (AM) or 3D printing emerges as an innovative technology\textsuperscript{13–19} for producing bonded magnets of customized shapes in which computer-aided design models enable the deposition of three-dimensional layer-by-layer stacking of magnet-polymer composites. Hence, AM offers several processing advantages: it minimizes waste and hence it reduces the amount of critical rare earth magnet powders needed for printing, eliminates tooling needs, and accelerates time to market. From a materials processing perspective, AM offers additional flexibility of printing bonded magnets with different polymer media to enable improved thermal stability for applications.

Extrusion based AM, used in this work, offers low cost printing methodology over other AM approaches such as selective laser melting (SLM)\textsuperscript{20,21} and selective laser sintering (SLS).\textsuperscript{22,23} The extrusion-based process provides better polymer and magnetic filler mixing which leads to better mechanical properties, corrosion resistance, and higher loading of magnetic fillers, hence results in higher energy product bonded magnets. Moreover, extrusion-based AM helps to avoid decomposition of SmFeN and resultant decrease in magnetization that would arise due to the heat from high energy laser processes like SLS. Considering the main challenges for bonded magnets manufacturing through AM, anisotropic SmFeN powder in PA12 polymer matrix are investigated in this study. Microstructural, magnetic properties and mechanical property of printed SmFeN nylon bonded magnets were characterized in detail.

\section{EXPERIMENTAL PROCEDURE}

Composite pellets of compounded Sm–Fe–N (Wellmax S3A-14 M grade of Sumitomo Metal Mining Co. Ltd.) in nylon PA12 were used for 3D printing via the fused deposition modeling, namely Big Area Additive Manufacturing (BAAM) process. Details of the BAAM process and post-printing magnetic field alignment have been previously discussed.\textsuperscript{14,15,17} The magnetic properties of both the as-printed and post-printing aligned SmFeN nylon bonded magnets were measured at 300 K using a Quantum Design SQUID magnetometer. Microstructures of the SmFeN nylon bonded magnets were examined by scanning electron microscopy (SEM) (Model: FEI Teneo). X-ray powder diffraction of the as-printed bonded magnets was performed with a Bruker diffractometer using Cu-K\textsubscript{\(\alpha\)} radiation and mechanical properties were evaluated on tensile testing of SS3 ASTM standard dog bone specimen samples along the printing direction. Details of the measurement techniques were reported earlier.\textsuperscript{14,15}

\section{RESULTS AND DISCUSSION}

\subsection{Microstructure}

Figure 1 shows the photograph of the as-printed magnets and the SEM images of the as-printed bonded magnet that reveals the morphology of the anisotropic Sm–Fe–N powder in PA12 matrix. As shown in Figure 1B, the average particle size of SmFeN magnet powder is 3 \(\mu\)m in a PA12 polymer matrix with no significant voids or cracks. It is known that the particle size and shape can affect the viscosity of the bonded magnets.\textsuperscript{19,24} For example, the orientation of the high aspect ratio particles have an effect on the overall viscosity of the samples since the particles tend to align along the shear plane. It is reported that non-spherical NdFeB suspensions generally have higher viscosities than that of the spherical NdFeB suspensions.\textsuperscript{24–26} Therefore, the particle shape and size could not only affect the rheology of the binder but also the loading fraction in the polymer thereby altering the magnetic and mechanical properties and also thermal stability of the bonded permanent magnets.

The structure of 3D printed SmFeN bonded magnets in PA12 was determined by XRD (Figure 2). Unlike other 3D metal printing techniques,\textsuperscript{27,28} only the Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{3} phase was observed with no undesired Sm–N, \(\alpha\)-Fe and oxide phases. The space group was determined to be R-3 m h (166), with lattice constants of \(a = b = 8.7248\) Å and \(c = 12.7120\) Å. Therefore it can be concluded that the additive printing did not degrade the Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{3} magnet powder.
FIGURE 1  (A) As-printed image and (B) SEM images of the as-printed SmFeN nylon bonded magnets

FIGURE 2  X-ray powder diffraction patterns of the as-printed SmFeN nylon bonded magnets

3.2  Magnetic properties

The magnetic hysteresis loops of the as-printed and post-printing aligned SmFeN nylon bonded magnets measured parallel to the alignment direction, at different magnetic field strengths are reported in Figure 3. The minimum field to align the magnetic particles was determined by applying an external magnetic field with varying strengths (µ0H = 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 T) as the printed magnets were heated from 300 to 550 K with a residence time of 15 min at 550 K, and then cooled to 300 K. The magnetic hysteresis loops were measured at 300 K before and after the alignment process. A significant increase in the remanence and a slight decrease in coercivity were observed with increasing magnetic field strength. The concentration of particles loaded in a polymer affects the magnetic properties of the bonded magnet. The saturation magnetization directly increases with higher loading of SmFeN magnet fraction and the effect of the magnetic field during alignment thereby increases the $B_r$ and $M_s$. Several factors can affect coercivity of the bonded magnets, namely the increase in dipole interaction due to high magnetic fraction content, and the changes in the degree of magnetic grain alignment leading to plausible cause for the reduction in coercivity.24,29

The magnetic properties of the anisotropic SmFeN nylon bonded magnets as a function of magnetic alignment fields is reported in Table 1. The as-printed magnets have a low remanence, $B_r = 0.35$ T, and higher coercivity, $H_c = 557$ kA m$^{-1}$. For the $µ_0H = 1.0$ T alignment field, the remanence of the magnet (0.67 T) is much higher, indicating the high degree of grain alignment of the SmFeN magnet powders. Although the coercivity (501 kA m$^{-1}$) is slightly less, an enhanced $(BH)_{max}$ of 75.6 KJ m$^{-3}$ is achieved, compared to that of the no-field and $µ_0H = 0.5$ T alignment field samples. For alignment magnetic field strengths above $µ_0H = 1$ T, the coercivity remains unchanged at 501 kA m$^{-1}$ while $B_r$ and $(BH)_{max}$ slightly improved to $\sim 0.68$ T and 78.8 KJ m$^{-3}$. For example, increasing the applied alignment field from $µ_0H = 1$ T to 3 T yielded $\sim 1.5\%$ increase in $B_r$. However the percentage increase in $(BH)_{max}$ is higher ($\sim 4.2\%$) due to the increased $B_r$ and resultant improved squareness of the hysteresis loop.

The attainment of remanence values as high as 0.68 T KG and coercivity as high as 501.3 kA m$^{-1}$, with energy products approaching 78.8 KJ m$^{-3}$, is highly significant in an additively manufactured Sm–Fe–N magnet, considering that one of
FIGURE 3  Magnetic hysteresis loops of the as-printed, and post-aligned SmFeN nylon bonded magnets (with varying magnetic field strengths of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 T)

TABLE 1  Magnetic properties of BAAM printed SmFeN nylon bonded magnets

| Alignment field (T) | Hc (kA/m) | Br (T) | (BH)max (KJ/m³) |
|---------------------|-----------|--------|-----------------|
| No field            | 557       | 0.35   | 20.1            |
| 0.5                 | 588.8     | 0.485  | 39.5            |
| 1.0                 | 501.3     | 0.67   | 75.6            |
| 1.5                 | 501.3     | 0.67   | 76.4            |
| 2.0                 | 501.3     | 0.673  | 77.2            |
| 2.5                 | 501.3     | 0.676  | 78.0            |
| 3.0                 | 501.3     | 0.68   | 78.8            |

the constituent magnet powders, the Sumitomo Wellmax 14 M, is rated to just 111.4 KJ m⁻³ with remanence under 0.8 T. Our additively manufactured magnets are achieving over 70% of rated performance of the powders, measured as energy product, and over 80% of rated remanence.

3.3  Mechanical properties

The mechanical properties of the BAAM printed SmFeN magnets are vital for their performance. Figure 4 presents the room temperature tensile stress data for the magnets. Four ASTM standard dog-bone shaped specimens were measured to determine the mechanical properties. Note that the “tails” at the start of the curve in Figure 3 are associated with the test conditions. The nature of the tensile profile of the sample exhibits three major regions before the ultimate breakage as shown in Figure 4. The initial inclined region is a regular extension of composite with stress. The predominant constant stress between 0.5% to up to 3% extension in two samples is the rotation of anisotropic particles in the pulling direction with maximum shear stress. The unusually long plateau might be the resulting effect of crushing of some large Sm₂Fe₁₇N₃ particles and shearing of nylon due to the anisotropic shape of magnetic fillers. The final elastic stage is the inclined straight-line section extracting the ultimate strength and Young’s modulus. The major mechanical parameters and average for all the samples is shown in Table 2. The ultimate strength greatly varies between 6 to 12 MPa which we believe are the two limits of isotropic NdFeB nylon¹⁵ and anisotropic NdFeB nylon¹⁴ BAAM magnets.

Sm₂Fe₁₇N₃ has been known since its original discovery by Coey et al. some 30 years ago,³⁰ as a magnetic material that has not achieved its full potential of energy products that rivals that of Nd₂Fe₁₄B, due to its instability at high-temperature which impedes sintering. High temperature sintering of Sm₂Fe₁₇N₃ decomposes the parent compound with removal of
FIGURE 4  Mechanical properties of the BAAM printed SmFeN nylon magnets. Tensile stress displacement curves of the BAAM printed SmFeN magnets; the inset shows the images of the four samples after tensile testing indicating the location of the breakage of the samples.

TABLE 2  Tensile parameters for BAAM printed SmFeN nylon magnets

| Sample # | Yield tensile strength (MPa) | Yield tensile strain % | Ultimate tensile strength (MPa) | Ultimate tensile strain % | Young’s modulus (GPa) |
|----------|-----------------------------|------------------------|--------------------------------|---------------------------|-----------------------|
| 1        | 10.439                      | 0.95                   | 12.480                         | 1.05                      | 1.378                 |
| 2        | 3.723                       | 3.21                   | 6.240                          | 3.32                      | 0.667                 |
| 3        | 7.108                       | 0.83                   | 9.142                          | 1.20                      | 1.105                 |
| 4        | 3.689                       | 3.98                   | 12.335                         | 4.01                      | 0.641                 |
| Average  | 5.661                       | 2.2                    | 8.784                          | 2.38                      | 0.853                 |

nitrogen from the structure. One of the potential methods of enhancing the thermal stability is introducing a chemical dopant which in most of the cases tends to be nonmagnetic dopant thereby decreasing both the saturation magnetization and Curie temperature of the magnet. Ultimately, this doping process decreases the overall energy product of the magnet. Recent first principles calculations\textsuperscript{31} suggest substitutions such as La or Ce may enhance its high-temperature stability while maintaining relevant magnetic properties (in particular, sufficient magnetic anisotropy). Such effects, if experimentally confirmed, would presumably persist to additively manufactured magnets as considered here, and would offer the promise of an alternative family of permanent magnets with performance, for both sintered and bonded magnets, comparable to that of Nd\textsubscript{2}Fe\textsubscript{14}B. This would be an important step, both for magnet development as well as resource criticality, given the present underutilization of Sm, which effectively increases the cost and criticality of the more commonly used Nd and Dy. However, polymer binders, as herein used, provide both stability and corrosion resistance to the printed SmFeN magnets up to the melting points of the individual polymers. Typically, nylon based printed magnets provide stability of up to 150°C operating temperatures\textsuperscript{14,15,17} and polyphenylene sulfide (PPS) polymers provide stability of up to 175°C–200°C operating temperatures.\textsuperscript{16}

4  CONCLUSION

This article presents AM fabrication and characterization of the magnetic and mechanical properties of BAAM printed anisotropic SmFeN based magnets in nylon (PA12) polymer. Phase analysis of AM printed bonded magnet by XRD indicates that there is no change of the SmFeN phase after 3D printing. An enhanced remanence of ~0.68 T and coercivity of 501.3 kA m\textsuperscript{−1} is achieved after optimizing post-printing alignment. The maximum energy product achieved for additively printed anisotropic bonded magnet of SmFeN in PA12 polymer is 78.8 KJ m\textsuperscript{−3}. AM offers the advantage for SmFeN bonded magnets manufacturing that enables efficient use of rare earth elements thus contributing towards addressing the reduced use of critical materials.
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CONFLICT OF INTEREST
All authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS
Kinjal Gandha: Data curation (equal); formal analysis (equal); methodology (equal); writing – original draft (equal); writing – review and editing (equal). Mariappan Parans Paranthaman: Conceptualization (equal); investigation (equal); methodology (equal); project administration (equal); writing – review and editing (equal). Brian C Sales: Data curation (equal); formal analysis (equal); methodology (equal); writing – original draft (equal). Haobo Wang: Data curation (equal); formal analysis (equal); methodology (equal); writing – original draft (equal). Adrian Dalagan: Data curation (equal); formal analysis (equal); methodology (equal); writing – original draft (equal). Tej N Lamichhane: Data curation (equal); formal analysis (equal); methodology (equal); writing – original draft (equal). Ikenna C Niebedim: Conceptualization (equal); investigation (equal); project administration (equal); supervision (equal); writing – review and editing (equal).

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available form the corresponding author upon reasonable request.

PEER REVIEW
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