Additive manufacturing of highly dense anisotropic Nd-Fe-B bonded magnets

Kinjal Gandha[a], Ikenna C. Nlebedim[a*], Vlastimil Kunc[b], Edgar Lara-Curzio[b], Robert Fredette[c], M. Parans Paranthaman[b*]

[a] Critical Materials Institute, Ames Laboratory, Ames, IA 50011, USA

[b] Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[c] Magnet Applications Inc., DuBois, PA 15801, USA

Extrusion based big area additive manufacturing process is utilized for fabrication of dense anisotropic bonded magnets. High loading fraction (≥70 vol.%) of magnequench anisotropic Nd-Fe-B powder in nylon is used for preparing anisotropic bonded magnets. A higher energy product of ~143.2 kJ/m^3 is obtained for the post printed magnetic field aligned at 1 Tesla. These findings make an important step towards the fabrication of gap magnets with energy product between ferrite and Nd-Fe-B sintered magnets. Moreover, printed bonded magnets exhibited better thermal stability, mechanical properties and superior magnetic properties compared to commercial injection molded magnets.

Keywords: Additive Manufacturing, Bonded Permanent Magnets, Anisotropic NdFeB, Gap Magnets, Mechanical Properties.

*Corresponding authors:
E-mail addresses: nlebedim@ameslab.gov (I.C. Nlebedim), paranthamanm@ornl.gov (M.P. Paranthaman).

Bonded magnets with moderate energy products and high coercivity (H_c) can have useful applications in devices e.g. small electric motors.[1, 2] Bonded Nd-Fe-B magnets have potentials as gap magnets, compared to lower energy product ferrites and AlNiCo magnets.[3-5] There are two principal approaches for manufacturing rare earth bonded magnets; compression and injection molding processes. Compression molding often enables higher loading fraction, hence increases the potential for maximum energy product (BH_{max}) compared to injection molding. However, injection molding enables processing flexibility in which complex and near net-shape magnets can be molded, thereby simplifying product assembly lines and accelerating prototyping.[6] However, the tooling costs of injection molding are higher than compression molding which is typically limited to more basic shapes due to the nature of the die-pressing process. Therefore, any improvements in processing methods are crucial in order to reduce production costs of bonded magnets while achieving superior magnetic, mechanical and, thermal properties.[7, 8]

Innovative developments in additive manufacturing (AM) have renewed research interest in the manufacturing of bonded Nd-Fe-B magnets.[9-13] It offers several processing advantages: it minimizes waste, eliminates tooling needs, accelerates time to market and can potentially reduce the overall cost of the magnets. In addition, near-net shape geometries can be printed even for bonded magnets of large sizes and complex shapes. In addition, energy density (BH_{max}) of printed bonded magnets have increased each year due to the new capabilities offered by AM. Therefore, AM of permanent magnets is of great interest to industry and scientific community.[13]

Our recent efforts in this emerging paradigm is focused on using AM for the development and optimization of the bonded magnetic materials.[14-16] Li et.al. demonstrated an extrusion-based 3D printing method to fabricate nylon bonded magnets using 65 vol.% isotropic Nd-Fe-B powders. The magnets exhibited lower porosity (8%) with superior magnetic properties (BH_{max}) = 43.76 kJ/m^3 compared to magnets prepared from other AM methods, including fused deposition modeling, binder-jet, and direct write.[17-20] Because the energy density is directly proportional to the square of the volume of the magnet powder present in bonded magnets, further increase in the magnet loading fraction is essential for achieving better magnetic performance.[21] Recently, Li et. al. also used isotropic Nd-Fe-B powder with high loading fraction of 70 vol. % to fabricate bonded magnets resulting in an increased BH_{max} 58.09 kJ/m^3.[15] Additional improvements in the magnetic performance of the bonded magnet can be realized by using anisotropic powders since it can result in higher remanence (B_r) and BH_{max}, than isotropic bonded magnets. Recently, we reported bonded magnets developed with 65 vol.% anisotropic hybrid composite powders of Dy-free magfine Nd-Fe-B and Sm-Fe-N with enhanced BH_{max} 89.92 kJ/m^3. We also studied the effects of various post-printing alignment with different magnetic field intensities and temperatures. In this work, we undertake an ambitious goal of producing anisotropic Nd-Fe-B bonded magnet with energy density that approaches the 119.36-159.15 kJ/m^3 gap magnet range by AM process. Our approach is to integrate the advantages of high loading fraction and the use anisotropic powder to accomplish higher BH_{max}. Here, we report the magnetic and mechanical properties of ≥70 vol.% Big Area Additive Manufacturing (BAAM) printed anisotropic magnets.

Composite pellets of 70 vol.% anisotropic MQA powder and 30 vol.% nylon-12, prepared by Magnet Applications Inc., were used for 3D printing via the BAAM process. Details of the preparation composite pellets and the BAAM process have been previously discussed.[17] Post-printing magnetic field alignment was afterwards performed up to an applied external magnetic field ($\mu_0 H_{ext}$) of 3.0 T. Samples were heated in magnetic fields of $\mu_0 H_{ext}$ = 0.25, 0.5, 0.75, 1.0, 2.0 and 3.0 T, and from 300 to 550 K with a dwell time of 15 min at 550 K, and then cooling to 300 K. After each alignment process, the magnetic hysteresis loops were measured again at 300 K.

The magnetic hysteresis loops of both as-printed randomly oriented and post-aligned bonded magnets along easy axis (parallel) were measured at 300 K using a Quantum Design SQUID magnetometer. Morphologies of the bonded magnets were examined by scanning electron microscopy (FEI Teneo LoVac). The crystalline structure was characterized by a Bruker X-ray diffractometer (XRD) using Cu K_α radiation. The mechanical properties of the sample were evaluated on tensile test specimen (SS3 ASTM standard dog bone design) which were aligned along the deposition direction. Details of the measurements were reported previously. [15,17]

Two different shapes of Nd-Fe-B bonded magnets, rectangular and hollow cylinder, printed in the BAAM system are shown in Fig. 1(a). The nominal dimensions of the magnets are 127 mm x 76.2 mm x 76.2 mm (LxWxH), for the rectangular magnet and 76.2 mm x 63.5 x 76.2 mm (OD, ID, H) for the hollow cylinder. The measured density of the whole square magnet piece is 5.15 g/cm^3. This study presents a promising method to fabricate large near-net shaped NdFeB bonded magnets through a BAAM process.

The loading fraction of Nd-Fe-B powder in the bonded magnet plays an important role in determining the magnetic properties. A higher volume loading fraction of Nd-Fe-B powder can be predicted to yield a higher B_r and BH_{max} which are desirable in high performance applications. Fig. 1b shows the room temperature magnetic hysteresis loops of the as-printed and post-aligned magnets at field strengths of $\mu_0 H_{ext}$ = 0.25, 0.5, 0.75, 1.0, 2.0 and 3.0 T. For the aligned samples, hysteresis loops were obtained parallel to the alignment direction assuming a demagnetization factor of N = 0.14 for the rectangular piece with dimensions LxWxH (4.5 x 1.5 x 1.5) mm^3. In the isotropic state (i.e. for the as-printed samples) B_r = 0.48 T and H_c = 962.88 kA/m were obtained. A significant increase in magnetic performance was observed after alignment, as summarized in Table 1 with data extracted from Fig. 1b. At low alignment field of $\mu_0 H_{ext}$ = 0.25 T, both B_r and BH_{max} increased to 0.8 T and 100.26 kJ/m^3, respectively while coercivity remained nearly the same. With increasing alignment magnetic field, the B_r increases and reaches a peak of 0.98 T for alignment at $\mu_0 H_{ext}$ = 2 T. The lower value of B_r obtained at $\mu_0 H_{ext}$ = 3 T, compared to that at $\mu_0 H_{ext}$ = 2 T is likely due to non-uniformity in loading fractions, as will be later explained. As expected, the same trend as in B_r is obtained in BH_{max}, hence the sample aligned at maximum applied field of $\mu_0 H_{ext}$ = 2 T has the highest BH_{max} of 148.01 kJ/m^3. H_c also remained fairly unchanged except for $\mu_0 H_{ext}$ = 1 T at which coercivity of 1034.5 kA/m was obtained. The results obtained in the present work agree with our previous work where we reported that a magnetic field of 1 T is sufficient to align anisotropic MQA magnet powders in bonded magnets.[22] Even though the coercivity is nearly unaffected by loading fraction of the particles in the binder, the magnetization is diluted and hence higher loading is essential for higher energy product.

To validate that the deviation of the B_r and BH_{max} in the aligned magnets could be due to the variation in the fraction of magnetic powder in the polymer, two more samples selected from the same piece were aligned at $\mu_0 H_{ext}$ = 0.75 T. Considering the ease of manufacturing, alignment fields below $\mu_0 H_{ext}$ = 1 T can be more practically realized. Fig. 1c shows the room temperature magnetic hysteresis loops of the three magnets aligned, labelled as sample 1, sample 2 and sample

3. The coercivity remained fairly constant for all samples. However, the B_r varied from 0.9 – 1.0 T and the BH_{max} varied from 132.1 to 158.35 kJ/m^3. Since the BH_{max} is proportional to the square of magnetic loading fraction, it is obvious that small section of the samples used for measurements contained more than 70 vol.% of MQA in nylon. Obtaining 158.35 kJ/m^3 in one of the sample indicates that that there is still room to increase the loading fraction, hence the BH_{max} of additively printed bonded magnets.

High temperature magnetic properties were studied to understand any effect of higher loading fraction on performance of bonded magnets at elevated temperatures. Thermal stability of the printed magnet was characterized by obtaining the reversible temperature coefficients of remanence, α, and the reversible thermal coefficient of coercivity, β. These parameters represent the rate of change in B_r and H_c, respectively, with temperature $\alpha = -0.09\%/K$ and $\beta = -0.53\%/K$, were calculated between 300 and 373 K. We observe that BAAM printed magnet showed thermal performance comparable to commercial injection molded magnets.

To verify the effect of magnetic field on the alignment of Nd-Fe-B powder particles in bonded magnets, the X-ray powder diffraction (XRD) patterns of the as-printed and post-printing aligned magnets cubes with dimensions of~5.6×5.6×5.6 mm^3 are reported in Fig. 2a. XRD spectra for post-printing aligned magnets were measured along the directions parallel to the c-axis. It can be seen that the composite magnet is crystalline and consists of only $Nd_2Fe_{14}B$ phase which crystallizes in the tetragonal crystal structure with space group $P4_2/mnm$. The intensity of the (0 0 4), (0 0 6), (0 0 8) peaks relative to the other peaks is higher in the aligned sample, compared to the as-printed sample which indicates strong texture due to alignment of magnetic easy axes.

SEM micrographs of the as-printed BAAM magnets and post printing aligned magnets cubes with dimensions of~5.6×5.6×5.6 mm^3 are shown in Fig. 2b and 2c. It can be seen that the magnets contain non-homogenous arbitrarily shaped particles with sizes between 100 - 200 μm (Fig. 2b). It is known that higher loading can be achieved by using powders of different sizes similar in design filled by the vacancies in the Bernal structure.[21] In the present case, higher loading of 70vol.% obtained is due to the presence of different particle sizes. It can be seen in Fig. 2c that particles or grain boundaries are oriented and formed a chain-like structure stacked along the field direction after post-printing alignment which resulted in the enhanced magnetic properties.

The impact of Nd-Fe-B powder volume fraction on the mechanical strength of bonded magnets have been studied. The room temperature tensile stress vs displacement curves of BAAM fabricated Nd-Fe-B magnets are shown in Fig.3. Four dog-bone shaped specimens were tested in order to determine the degree of variability in mechanical properties between samples. The stress-displacement profile of the nylon-bonded in-situ field-aligned AM printed magnet indicates more brittle nature than isotropic nylon-bonded magnets. [15] This behavior can be expected because of the unimodal distribution of particles. The initial extension of the magnet without much increase in tensile stress shown in Fig. 3 corresponds to removal of slack when the edges of the test specimen are in full contact with the grips. The average ultimate tensile strength was 14.2 MPa. Details of each sample are listed in Table 3. BAAM printed bonded magnets prepared using 65 vol.% isotropic NdFeB powder have resulted in tensile strength of 6.6 MPa.[17] It has been reported that higher loading fraction of NdFeB powder in Nylon binder can result in enhanced mechanical properties. [23] The improved tensile strength by ~73% can be due to higher loading fraction of 70 vol.% of powder into the binder.

Our recent development and progress in additve printing of both isotropic and anisotropic magnets of different loading fractions and energy products are shown in Fig. 4. BAAM fabricated isotropic magnets with 65 vol.% had BH_{max} of 43.76 kJ/m^3. An increase in loading fraction of up to 70 vol.% led to BH_{max} of 58.09 kJ/m^3, a 33% increase in BH_{max}.[15] Anistropic bonded magnets with 65 vol.% loading fraction led to BH_{max} of 89.92 kJ/m^3.[14] A 107% increase in BH_{max} was obtained with same loading fraction (65 vol.%) for anisotropic powder, compared to isotropic powders. In this work, ≥70 vol.% of anisotropic Nd-Fe-B powder led to a BH_{max} of ~143.2 – 151.2 kJ/m^3. The images of both as-printed (A) – (D) and corresponding post-annealed (A1) – (D1) 70 vol.% anisotropic Nd-Fe-B bonded magnets with LxWxH dimensions ~9.2 × 8.5×6.5 mm^3 at 520 K and different field strengths of 0.25 T; 0.5 T; 0.75 T; and 1.0 T are shown in Fig.S1 (supplementary material). These images show that the printed magnets maintain the shapes even after post-annealing. This indicates that enhanced magnetic properties of BAAM printed magnets can rival injection molded magnets due to potential to the processing benefits offered by additive manufacturing. Our work shows that additive manufacturing can enable production of gap magnets for different applications.

The magnetic properties and thermal stability of the BAAM printed bonded magnets are investigated and compared with commercial traditional aligned injection molded magnet made from the same starting MQA anisotropic powder in Table 4. The BAAM printing process enables higher loading fraction (70 vol.%) in bonded magnets compared to those of traditional injection molded magnets (54 vol.%).[24] In addition there is a substantial improvement in energy product and remanance obtained with the BAAM printed bonded magnets. The energy product and remanence improved by 100% and 48% respectively.

In summary, anisotropic nylon bonded Nd-Fe-B magnets with a high loading fraction of ≥70 vol.% were fabricated via an extrusion-based additive manufacturing process. A higher energy product of ~143.2 kJ/m^3 was obtained with alignment at 1.0 T field. The BAAM printed magnets exhibited good thermal stability, mechanical properties and superior magnetic properties such as high BH_{max} and B_r, compared to commercial injection molded magnets. This work demonstrates that additive manufacturing is a promising fabrication method towards the development of near-net shape gap magnets.

ACKNOWLEDGMENT

This research was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. Authors would like to thank Cincinnati Inc. for BAAM development.

REFERENCES

[1] H.J. Kim, C.S. Koh, P.S. Shin, IEEE Transactions on Magnetics 46(6) (2010) 2314-2317.
[2] F. Yamashita, A. Watanabe, H. Fukunaga, IEEE Transactions on Magnetics 39(5) (2003) 2980-2982.
[3] J. Herchenroeder, D. Miller, N.K. Sheth, M.C. Foo, K. Nagarathnam, Journal of Applied Physics 109(7) (2011) 07A743.
[4] T. Takeshita, K. Morimoto, Journal of Applied Physics 79(8) (1996) 5040-5044.
[5] N. Poudyal, V.V. Nguyen, C.-b. Rong, J.P. Liu, Journal of Physics D: Applied Physics 44(33) (2011) 335002.
[6] J. Ormerod, S. Constantinides, Journal of Applied Physics 81(8) (1997) 4816-4820.
[7] J.M.D. Coey, Solid State Communications 102(2) (1997) 101-105.
[8] D. Brown, B.-M. Ma, Z. Chen, Journal of Magnetism and Magnetic Materials 248(3) (2002) 432-440.
[9] M.P. Paranthaman, C.S. Shafer, A.M. Elliott, D.H. Siddel, M.A. McGuire, R.M. Springfield, J. Martin, R. Fredette, J. Ormerod, JOM 68(7) (2016) 1978-1982.
[10] C. Huber, C. Abert, F. Bruckner, M. Groenefeld, O. Muthsam, S. Schuschnigg, K. Sirak, R. Thanhoffer, I. Teliban, C. Vogler, R. Windl, D. Suess, Applied Physics Letters 109(16) (2016) 162401.
[11] L. Li, A. Tirado, B.S. Conner, M. Chi, A.M. Elliott, O. Rios, H. Zhou, M.P. Paranthaman, Journal of Magnetism and Magnetic Materials 438 (2017) 163-167.
[12] J. Jacimovic, F. Binda, L.G. Herrmann, F. Greuter, J. Genta, M. Calvo, T. Tomse, R.A. Simon, arXiv preprint arXiv:1611.05332 (2016).
[13] L. Li, B. Post, V. Kunc, A.M. Elliott, M.P. Paranthaman, Scripta Materialia 135 (2017) 100-104.
[14] K. Gandha, L. Li, I.C. Nlebedim, B.K. Post, V. Kunc, B.C. Sales, J. Bell, M.P. Paranthaman, Journal of Magnetism and Magnetic Materials 467 (2018) 8-13.
[15] L. Li, K. Jones, B. Sales, J.L. Pries, I.C. Nlebedim, K. Jin, H. Bei, B.K. Post, M.S. Kesler, O. Rios, V. Kunc, R. Fredette, J. Ormerod, A. Williams, T.A. Lograsso, M.P. Paranthaman, Additive Manufacturing 21 (2018) 495-500.
[16] K. Gandha, G. Ouyang, S. Gupta, V. Kunc, M. Parans Paranthaman, I.C. Nlebedim, Waste Management 90 (2019) 94-99.
[17] L. Li, A. Tirado, I. Nlebedim, O. Rios, B. Post, V. Kunc, R. Lowden, E. Lara-Curzio, R. Fredette, J. Ormerod, Scientific reports 6 (2016) 36212.
[18] A. Shen, C.P. Bailey, A.W.K. Ma, S. Dardona, Journal of Magnetism and Magnetic Materials 462 (2018) 220-225.
[19] S. Kim, F. Qiu, S. Kim, A. Ghanbari, C. Moon, L. Zhang, B.J. Nelson, H. Choi, Advanced Materials 25(41) (2013) 5863-5868.
[20] C. Huber, C. Abert, F. Bruckner, M. Groenefeld, S. Schuschnigg, I. Teliban, C. Vogler, G. Wautischer, R. Windl, D. Suess, Scientific Reports 7(1) (2017) 9419.
[21] J.M.D. Coey, K. O'Donnell, Journal of Applied Physics 81(8) (1997) 4810-4815.
[22] I.C. Nlebedim, H. Ucar, C.B. Hatter, R.W. McCallum, S.K. McCall, M.J. Kramer, M.P. Paranthaman, Journal of Magnetism and Magnetic Materials 422 (2017) 168-173.
[23] M.G. Garrell, A.J. Shih, B.-M. Ma, E. Lara-Curzio, R.O. Scattergood, Journal of Magnetism and Magnetic Materials 257(1) (2003) 32-43.
[24] Magnequench, MQA (Anisotropic Powder)<mqa-brochure.pdf>, 2017.

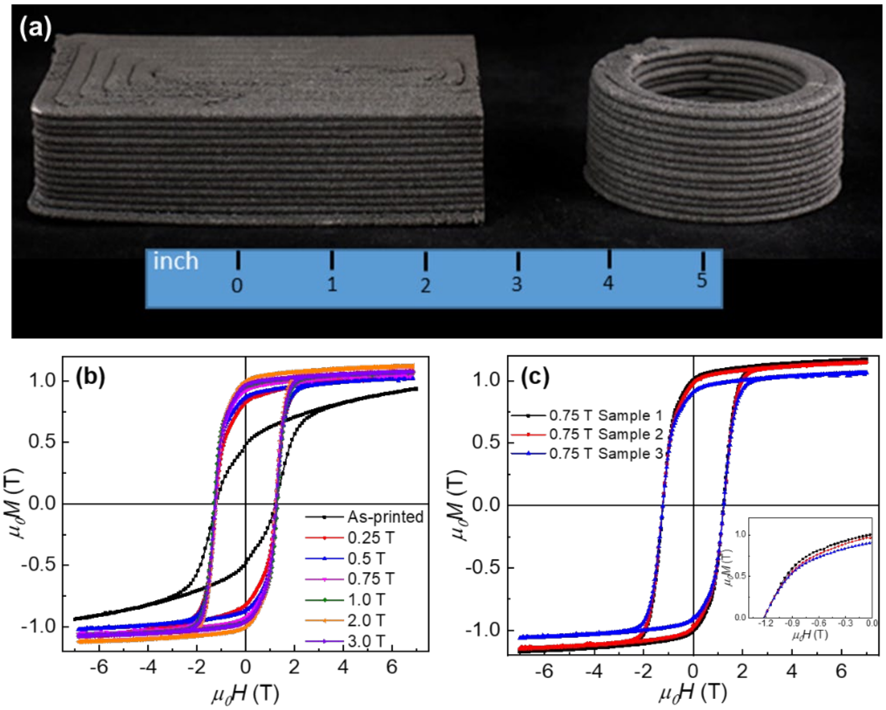

Fig. 1. (a) Image of near net-shaped Nd-Fe-B printed bonded magnets. (b) Room temperature hysteresis loops of the as-printed and post-aligned 70 vol.% anisotropic Nd-Fe-B bonded magnets at different field strength. (c) Room temperature hysteresis loops of the post-aligned 70 vol.% anisotropic Nd-Fe-B bonded magnets at 0.75 T. Inset second quadrant loops.

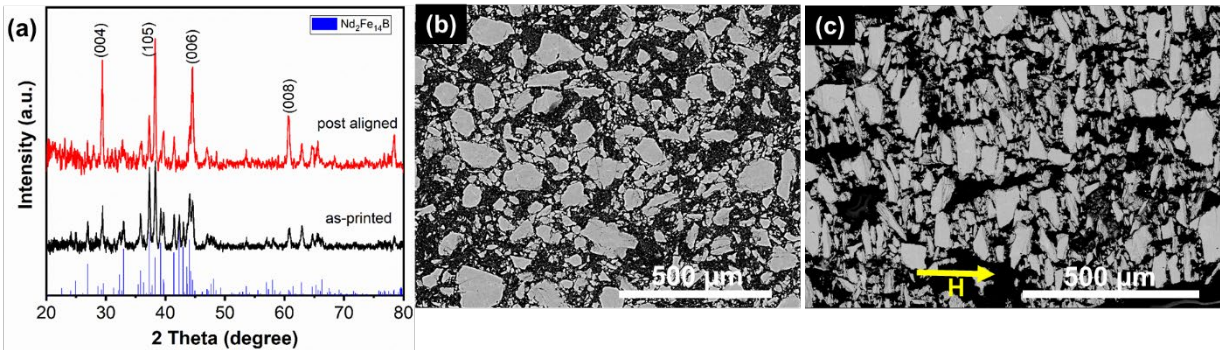

Fig. 2 (a) XRD patterns of the as-printed and post-aligned 70 vol.% anisotropic Nd-Fe-B bonded magnets at 1.0 T. SEM micrograph of the surface of the (b) as-printed BAAM magnets and, (c) Post aligned magnets at 1.0 T.

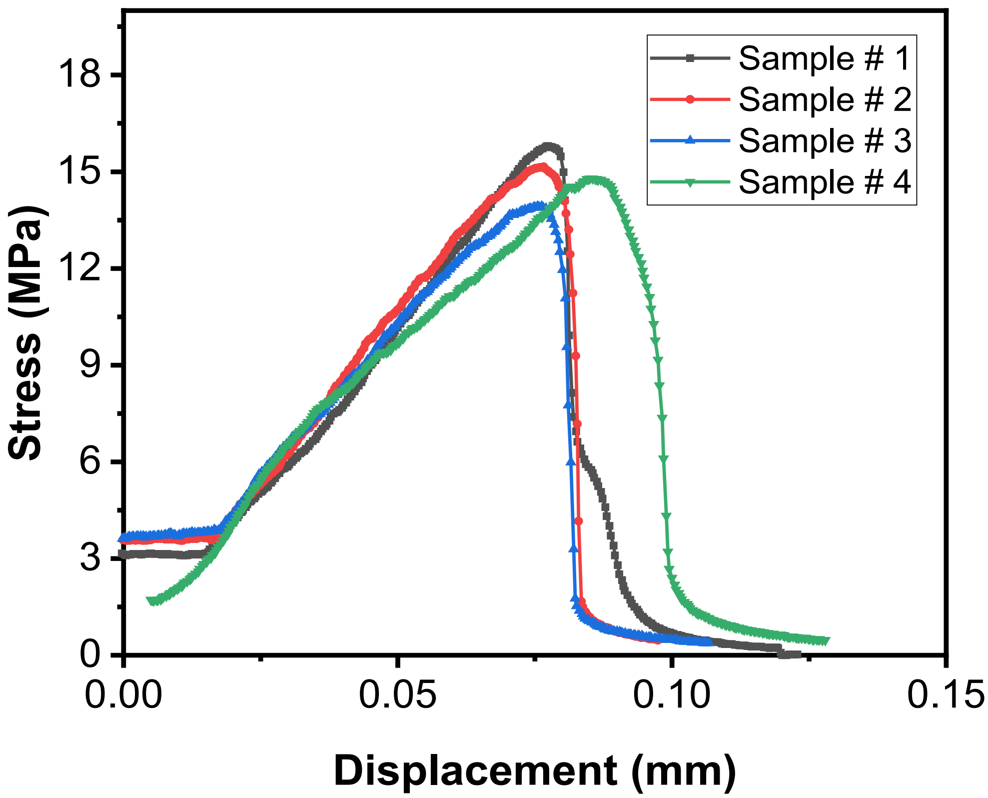

Fig. 3. Mechanical properties of the BAAM fabricated Nd-Fe-B magnets. Tensile stress-displacement curves of the BAAM fabricated Nd-Fe-B magnets. Samples 1, 2 and 3 show some degree of shear stress in the beginning. Then the linear segment represents the elastic limit followed by staggering plastic tails and breakage at the end.

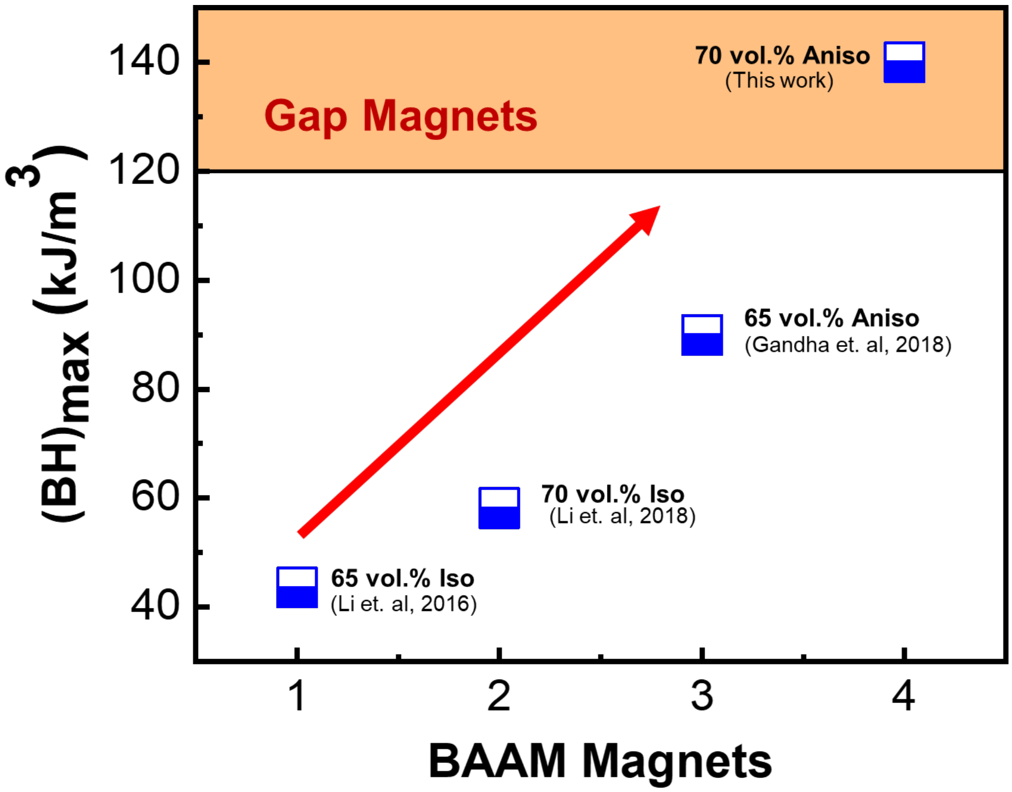

Fig. 4. Development in energy product, BH_{max} of additively manufactured bonded magnet using BAAM system.

Table 1: Magnetic properties of the as-printed and post-aligned BAAM fabricated bonded Nd-Fe-B magnet with dimensions LxWxH (4.5 x 1.5 x 1.5) mm^3 at different magnetic field strength along easy axis.

Alignment Field (T)	B_r **(T)**	H_c **(kA/m)**	BH_{max} **(kJ/m³)**
As-printed	0.48	962.88	35.0
0 .25	0.8	970.84	100.26
0.5	0.85	994.71	177.77
0.75	0.90	978.8	132.10
1.0	0.94	1034.5	140.05
2.0	0.98	978.8	148.81
3.0	0.94	994.71	139.26

Table 2: Magnetic properties of the post aligned LxWxH (4.5 x 1.5 x 1.5) mm^3 BAAM fabricated bonded Nd-Fe-B magnet at 0.75 T along easy axis.

Samples	H_c (kA/m)	B_r (T)	BH_{max} (kJ/m^3)
Sample # 1	970.84	1.0	158.35
Sample # 2	978.80	0.97	146.42
Sample # 3	978.80	0.90	132.10

Table 3: Mechanical properties of BAAM fabricated bonded Nd-Fe-B magnets measured at room temperature.

	Max Load (lbf)	**Max Stress (MPa)**
Sample # 1	9.23	14.77
Sample # 2	8.92	14.28
Sample # 3	8.20	13.12
Sample # 4	8.17	13.08

Table 4: Magnetic properties of MQA-38-14 commercial Injection Molded Magnet and BAAM fabricated bonded Nd-Fe-B magnets measured at room temperature.

	MQA-38-14 Magnet (Injection Molded 54 vol. % in PPS) [25]	**MQA-38-14 Magnet (BAAM Printed 70 vol. % in Nylon)**
B_r **(T)**	0.635	0.94
H_c **(kA/m)**	1082.2	1034.5
BH_{max} **(kJ/m³)**	70.0	140.0
α **to 373 K (100 °C)**	-0.09 %	-0.09%
β **to 373 K (100 °C)**	-0.66 %	-0.53 %

Supplementary Information

Additive manufacturing of highly dense anisotropic Nd-Fe-B bonded magnets

Kinjal Gandha[a], Ikenna C. Nlebedim[a*], Vlastimil Kunc[b], Edgar Lara-Curzio[b], Robert Fredette[c], M. Parans Paranthaman[b*]

[a] Critical Materials Institute, Ames Laboratory, Ames, IA 50011, USA

[b] Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[c] Magnet Applications Inc., DuBois, PA 15801, USA

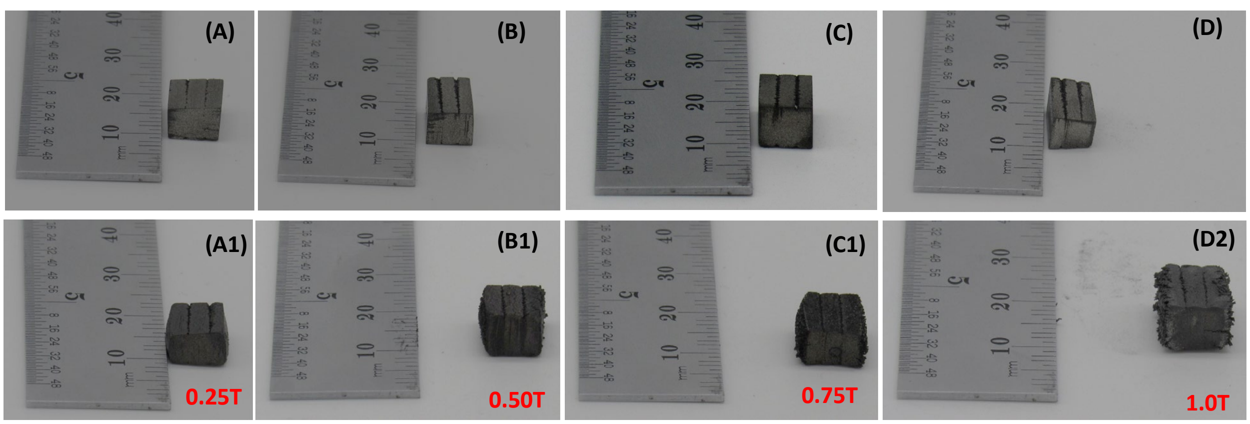

Fig. S1. Images of both as-printed (A) – (D) and corresponding post-annealed (A1) – (D1) 70 vol.% anisotropic Nd-Fe-B bonded magnets with LxWxH dimensions ~$9.2 \times 8.5 \times 6.5$ mm^3 at 520K and different field strength (marked in red).