This is the published version of a paper published in *Procedia Manufacturing*.

Citation for the original published paper (version of record):

Popov, V., Koptioug, A., Radulov, I., Maccari, F., Muller, G. (2018)
Prospects of additive manufacturing of rare-earth and non-rare-earth permanent magnets
*Procedia Manufacturing*, 21: 100-108
https://doi.org/10.1016/j.promfg.2018.02.199

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:miun:diva-34550
Prospects of additive manufacturing of rare-earth and non-rare-earth permanent magnets

Vladimir Popov\textsuperscript{a*}, Andrey Koptyug\textsuperscript{b}, Iliya Radulov\textsuperscript{c}, Fernando Maccari\textsuperscript{c}, Gary Muller\textsuperscript{a}

\textsuperscript{a}Israel Institute of Metals, Technion R&D Foundation, Technion City, 3200003, Haifa, Israel
\textsuperscript{b}Sports Tech Research Centre, Mid Sweden University, Akademigatan 1, SE-831 25, Östersund, Sweden
\textsuperscript{c}Technische Universität Darmstadt, Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany

Abstract

Additive manufacturing (AM) or 3D-printing started as a prototyping technique in plastic has succeeded in metals for life safety applications as airspace and medical implants production. Today having advantages in fabricating products of desired shape, geometry, lightweight structures and required mechanical properties, 3D-printing faces a new challenge – AM of permanent magnets (PM). 3D-printing significantly simplifies manufacturing of net-shape bonded magnets, simplifies the new phase magnets prototyping, and also enables efficient use of rare earth (RE) elements [1]. The major development nowadays is performed by AM of bonded Nd-Fe-B using different binders/polymers [1, 2]. 3D printing technologies of non-RE magnets are not so widely represented [3]. The AM of RE-free PM, such as Al-Ni-Co [4] and MnAl(C) [5], is also developed, because of their great benefit of being non-RE, presenting advantages of AM technology and sufficient magnetic properties. This work presents the state-of-the-art of 3D-printing of PM, including RE and RE-free, bonded and non-bonded magnets. Prospects of electron beam melting (EBM) of non-rare-earth MnAl(C) are shown.

© 2018 The Authors. Published by Elsevier B.V.
Peer-review under responsibility of the scientific committee of the 15th Global Conference on Sustainable Manufacturing (GCSM).

Keywords: 3D-Printing; additive manufacturing; permanent magnets; rare-earth magnets

1. Introduction

This paper gives an overview the state-of-the-art in the field of additive manufacturing of hard magnetic materials with and without rare-earth (RE) elements.

---

\* Corresponding author. Tel.: +972-53-3349153; fax +972-4-8294571.
E-mail address: vvp@technion.ac.il
Though the additive manufacturing of magnetic materials has just recently begun, it can already be said that this new fabrication method makes manufacturing of net-shape easier and use of critical RE materials more efficient.

The development of new magnetic materials is essential and indispensable for improving the efficiency and performance of devices in electric power generation, conditioning, conversion, transportation, and other energy-use sectors of economy. Functional magnetic materials, such as advanced hard and soft magnets, magnetic refrigerants, magnetic MEMS (microelectromechanical systems), magnetic shape memory alloys, and magnetorheological fluids and elastomers, substantially impact all contemporary energy-saving technologies. Among these classes of materials, advanced permanent magnets play an important role providing high efficiency and reliability and compact, low cost, and low maintenance solutions for renewable energy technologies, including wind turbines, hydroelectric power generators, and wave power buoys. The main attempts of permanent magnets printing are held with NdFeB magnets, because of its outstanding magnetic characteristics.

The industrial powder metallurgy process of permanent magnets made of NdFeB can be divided in 7 steps (Fig. 1a) concluding three basic stages: preparation of the powder, fabrication and post-processing.

The functional magnetic properties of permanent magnets are extrinsic in nature, depending on the particular microstructure developed during magnet processing. The magnetization reversal in NdFeB sintered magnets is known to start at the surface of main phase grains, and that is why the microstructure optimization in NdFeB-based sintered magnets involving grain size reduction and strain boundary engineering has been extensively investigated in the last few years. To counteract the magnetic reversal, a special microstructure has been developed (Fig. 1b). It consists of single crystalline Nd_{2}Fe_{14}B (grey on Fig. 1b) grains a size of 3-10 μm, surrounded by a continuous layer of amorphous Nd - rich phase (white regions on Fig. 1b) with a thickness of only a few nm and larger Nd - rich phases in the grain junctions. Each grain acts as an independent small magnet. The thin grain boundary smoothes the grain surfaces and eliminates to some extent the number of structural defects, which decreases the probability of nucleation of reversed domains. Furthermore, the grain boundary phase (GBP) magnetically decouples the grains, which prevents reversal “avalanches” within the magnet. The GBP is generally believed to be paramagnetic.

![Fig 1. (a) Production route of NdFeB sintered permanent magnets [6]. (b) SEM image of a typical microstructure of a sintered NdFeB permanent magnet. The faint bright contrast between the grains stems from the nanometer-sized grain boundary phase.](image)

The NdFeB magnets are currently produced at the industrial scale by the powder metallurgy route starting from micro-crystalline powders and involving liquid phase sintering step. Basically, the microstructure is made of individual crystallites, mainly of the Nd_{2}Fe_{14}B phase, and separated by nonmagnetic thin layers [7]. Nowadays it is believed that various kinds of internal defects, as well as the grain size and grain boundary dimensions, govern the
coercivity of sintered polycrystalline Nd$_3$Fe$_{14}$B [8]. The industrial sintering process of NdFeB permanent magnets is divided into 8 main parts, which are schematically depicted in Fig. 1a: An alloy of a desired composition is produced via a rapid solidification technique called “strip casting”, which is similar to melt-spinning, with less rapid cooling rates. Afterwards, the ingot is hydrogen-decapped, crushed, and milled into a fine powder. This powder consists now of single crystalline NdFeB particles of a size of 5-10 µm, which are filled in a press form, aligned in a magnetic field and pressed to the desired shape. The green compact is finally sintered and annealed at lower temperatures. A coating is applied to protect the magnet against corrosion.

Whereas with the sintering the minimum grain size is still limited to 1 mm, hot-deformation results in nanocrystalline magnets (grain size of 10-50 nm) with better thermal stability and corrosion resistance compared to their microcrystalline counterparts [9, 10]. For this technology the master alloy has to be arc-melted and subsequently melt-spun at a wheel speed of 20-50 m/s to obtain fine crystalline ribbons with optimized homogeneity. The as-obtained melt-spun ribbon powders can be milled in a planetary ball mill or jet mill. After that, a hot-compaction process at 700-750 °C and 50-200 MPa leads to fully dense nanocrystalline pellet.

Different techniques of 3D printing are developing in parallel trying to produce high performance NdFeB permanent magnets and other different magnetic materials for specific applications.

2. Promising approaches of additive manufacturing of permanent magnets

Thus, additive manufacturing of permanent magnets is of great interest for industry and scientific community. It concerns either bonded magnets, or polymer-free ones, with rare-earth materials or without them.

2.1. Fused deposition modeling of RE permanent magnets

Fused deposition modeling (FDM) is an extrusion/jetting based additive manufacturing process that actually utilizes thermoplastics, such as ABS, PLA, PETG etc. However, this technology is also applicable for permanent magnets fabrication. Dr. Süss and his colleagues from Vienna’s Technische Universität Wien (TU Wien) have demonstrated a way of printing bonded magnets that resembles the plastic-filament printers [11]. The wire-shaped thermoplastic filament contained 45-65% (by volume) of magnetic granules.

As the filament is melted, it is extruded by the printer to build a shape layer by layer. This permits the production of far more complex magnets than the injection molding can turn out. During the fabrication process the granules are in a non-magnetized state, but placing the printed magnet into a strong magnetic field converts it into a permanent magnet.

That opens up new possibilities, such as using different materials within a single magnet to create areas of strong and weak magnetism. This could be useful in certain types of sensors.

However, the injection-moulded magnet (prepared with mostly used polymer Polyamide 12 – PA 12) is limited in typical applications to only 120 – 140°C by thermal and mechanical properties of the polymer matrix, whereas 3D printing offers a much broader operation temperature range that makes these magnets suitable for highly demandable applications.

2.2. Big Area Additive Manufacturing of NdFeB bonded magnets

The new fabrication method for permanent NdFeB magnets – the Big Area Additive Manufacturing (BAAM), performed by Dr. Paranthaman [2] and his colleagues, is an original binder jetting technique that combines several unique advantages. BAAM is an industry scale rapid and cost efficient AM system. Dr. Paranthaman declares that this technology has been already successfully used in the past to print car bodies from a mixture of carbon fibre and plastic. Now BAAM is a technique for high performance NdFeB bonded magnets production. For the bonded magnets the AM traditionally used magnet powder with polymers (thermoset, thermoplastic, elastomer).

The BAAM technique is focused not only on the design benefits, but also on density increasing for an improvement of magnetic properties. The analysis of magnetic and metallurgical properties of the new 3d-printed magnets is presented in comparison with the sintered magnets, compression bonded and injection moulded bonded NdFeB.
magnets. The properties achieved in the BAAM magnets are: $BH_{\text{max}} = 5.47$ MGOe (against 4.55 MGOe for injection moulded magnets); Max operating temperature 150°C; Yong Modulus 4.29 GPa; Ultimate Tensile Strength 6.6 MPa; density 5.2 g/cm$^3$; 5% porosity level between layers. The researchers declared that the density can be additionally increased up to 30% by low melting alloy infiltration into binder jet NdFeB magnets.

The starting composite pellets for polymer magnets consisted of 65 vol% of isotropic NdFeB powder and 35 vol% of polyamide (Nylon-12). They demonstrated the following magnetic properties at room temperature: intrinsic coercivity $H_{\text{ci}} = 688.4$ kA/m, remanence $B_r = 5.1$ kG, and energy product $(BH)_{\text{max}} = 43.49$ kJ/m$^3$ (5.47 MGOe). The novel method considerably simplifies fabrication of net-shape bonded magnets. However, magnetization of these materials is unfortunately markedly lower than for polymer bounded magnets.

The microstructure dictates transference of the intrinsic features to the extrinsic properties, which describe the technical performance of PM. The reasons for NdFeB being magnetically hard lie in the peculiarities of its microstructure. In simple terms, the NdFeB permanent magnet should be multiphase (ferromagnetic Nd$_2$Fe$_{14}$B phase with high magnetization and high magnetic anisotropy + paramagnetic Nd-rich phase) and fine-grained.

The main reason why such relatively poor magnetic properties were obtained BAAM lies in the fact, that till now the only one known way to obtain reasonable coercivity in AM consists in the usage of rapidly quenched ribbons (with proper microstructure) and polymer binder. The direct usage of more advanced technique, as selective laser melting or electron beam melting will lead to new microstructures, ensuring higher coercivity of these materials.

However, BAAM technique saves the usage of RE-elements like Dy or Nd and reduces the cost of PM fabrication. The specific benefits of BAAM are the possibility to produce Gap magnets, to realize novel motor design and to reduce the time to market. Besides, the BAAM magnets don’t need any post annealing, just polishing.

2.3. Stereolithography of magnetic materials

Stereolithography apparatus (SLA), also known as optical fabrication or photo-solidification is a type AM technology used as photo-polymerization process, by which light causes chains of molecules to link, forming polymers. SLA works by focusing an ultraviolet (UV) laser on to a vat of photopolymer resin. The technology works with the help of computer aided design (CAD) software. The beam (UV or laser) draws the cross-section image of 3D-design on the surface of the resin/photopolymer vat. Resins/photopolymers are very sensitive to ultraviolet light, so they are photo-chemically solidified and form a single layer of the desired 3D object [12]. An elevator platform descends to a distance equal to the thickness of a single layer of the model (typically 0.05 mm to 0.15 mm) into a photopolymer vat. Then, a resin-filled blade sweeps throughout a cross section of the layer, re-coating it with fresh material. Then the subsequent layer is deposited, joining the previous layer, and thus a complete 3D object can be formed by this process. The designs are then immersed in a chemical bath to remove any excess resin and cured in an ultraviolet oven. An advantage of the SLA "bottom-up" mode is that the build volume can be much bigger than the vat itself, and only an enough amount of photopolymer is required to keep the bottom of the build vat continuously full of the photopolymer.
A method of stereolithographic production of a permanent magnet is described in [12]. The NdFeB permanent magnet was used to test the desired location of magnetic particles in a polymer printed part. A novel mask image projection stereolithography process with an external magnetic field was successfully developed for fabrication of magnetic-field responsive smart materials. Magnetic particles affected by an external magnetic field were selectively deposited in liquid resin and distributed in various patterns. The as-obtained mask image was then projected to cure the photopolymer filled with the magnetic particles. The process developed is capable of achieving various magnetic particle-filling rates, filling patterns and structures, thus enabling to produce smart materials with complicated and heterogeneous functions. As a concept-of-proof, three test cases have been performed. The shown [12] experimental results demonstrate the feasibility and effectiveness of the proposed magnetic field-assisted projection stereolithography (M-PSL) technique in fabrication of smart materials.

Stereolithography experiments performed at Technion are focused on magnetic and ceramic materials. One of the researched powders used for SLA-printing was MnAl(C) prepared at TU Darmstadt by milling. The prepared powder was distributed in the polymer resin in the printer's vat in proportion: 50% powder and 50% resin.

The preliminary printing experiments showed that the homogeneous dispersion of the powder in each layer is a challenge that should be worked out. In Fig. 2b it can be seen that a part of pieces were broke away. The reason for that is an extra content of powder in these parts, because of non-homogeneous distribution of the powder in resin.

2.4. Selective Laser Melting of NdFeB permanent magnets

Selective laser melting (SLM) is a well-known additive manufacturing technology which has at its disposal a great number of different approved powders: titanium and aluminum alloys; stainless steels; cobalt and nickel alloys, etc. Because of such great material base, the development of specific magnetic powders for SLM was just a question of time, and has already started.

Dr. Jacimovic and his colleagues from ABB, Switzerland for the first time performed the unconventional process, Selective Laser Melting (SLM), usually used for metals, to print net-shape RE permanent magnets of very fine microstructure [13], with stable magnetic performances up to elevated temperatures. In the framework of this research, a specific spherical powder suitable for the SLM process was selected, aiming to enable powder flowability necessary for homogenous and dense deposition of a powder bed on a start platform [13]. The as-printed Nd<sub>2</sub>Fe<sub>14</sub>B permanent magnet demonstrated very good magnetic properties of the as-printed samples without additional post heating treatment: Hc= 695 kA/m, Br = 0.59 T, (BH)max=45 kJ/m<sup>3</sup>. It can be explained by the fact that grain size of printed magnets was of only 1 μm, one order of magnitude lower than in sintered magnets [13].

![Fig. 2. (a) The MnAl(C) powder used in experiment (SEM); (b) the printed composite part contained resin and magnetic MnAl(C) powder.](image-url)
Another experiment production of magnetic materials by SLM is presented in [14]. Dr. Zhang et al. printed Fe-Ni Permalloy by the SLM. The used powder composition was Fe-80wt%Ni. However, the produced Fe-Ni Permalloy is a soft magnetic material.

These successful results illustrate not only applicability of the SLM for permanent magnets fabrication, but the potential of the technology to produce magnets with controlled microstructure and magnetic properties, using the laser machine settings.

2.5. Selective Laser Melting of Al-Ni-Co permanent magnets

Net-shape processing of Al-Ni-Co magnets reported in [4] is also of great interest because of combining benefits of AM and the use of non-RE permanent magnets. Such alternatives to RE permanent magnets may decrease the cost of PM for such applications as electrical motors. Emma White from AMES Laboratory, USA, successfully produced Al-Ni-Co magnets by AM using a laser engineered net shaping (LENS) system. For the AM a modified Al-Ni-Co high-pressure gas atomized spherical powder with low oxygen content was used. Manufactured alnico parts were heat-treated in different conditions. Magnetic structure is very sensitive to magnetic annealing time and temperature.

The magnetic properties showed improvement over their cast and sintered counterparts. The Al-Ni-Co printed parts showed remanence values up to 9.0 kG that approaches the 10.6 kG of the directionally solidified, highly textured, anisotropic cast Al-Ni-Co. The samples produced by AMES Laboratory had coercivity of 2.03 kOe, which is higher than that of sintered Al-Ni-Co [4]. The results obtained by Emma White also show possibilities for the AM not only to reduce the processing and post processing costs, but also to improve properties by squaring the hysteresis loop. These results indicate that the AM processing is a perspective technique method of fabrication Al-Ni-Co permanent magnets with high coercivity. The new fabrication approach demonstrates promising prospects of additive manufactured Al-Ni-Co magnets for next generation electrical motors and other applications requiring complex engineered part geometries.
2.6. Electron Beam Melting of MnAl(C) magnets

Vacuum environment and high temperature conditions of electron beam melting (EBM©) AM seem to be effective and suitable for PM production. However, until now no significant attempts to manufacture magnetic materials by EBM were reported. Arcam EBM© systems utilize a high power electron beam that provides the energy needed for high melting capacity and high productivity.

Vacuum environment and powder layer pre-heating is favorable for manufacturing alloys sensitive to oxidation and dissolved gas. Melting carried out layer by layer at controlled elevated temperature allowing for low residual stress of manufactured components. Because of the fast dynamics of the melt point (melting – solidification) unique crystalline microstructure of the resulting material can be reached [15]. However, the list of certificated powders for EBM© is relatively small, and there are no any certificated magnetic materials powders yet.

It is known, that varying processing conditions in EBM© it is possible to significantly vary the material microstructure [16], including producing metastable states. For example, successful manufacturing of bulk metallic glasses by EBM© is already proven [17]. In such case all built area is kept at much lower temperature than usual.
processing temperatures (below glass transition point). These considerations point out to obvious possibilities for processing of materials for PM.

Initial joint experiments were carried out to confirm prospects of the EBM© technology for PM production. At Sports Tech Research Center (STRC Sweden) the EBM© printing of set of samples from MnAl(C) powder, provided by TU Darmstadt, was performed (Fig.3).

Preparatory work included powder flowability tests, powder sintering tests (Fig. 3b) and search of optimal process parameters settings. For EBM© production of new MnAl(C) printed samples (Fig. 3c), the modified table system with small round start platform was used (Fig. 3a). The diameter of start platform was 80 mm. The set of parameters used for electron beam melting was performed based on already known Ti-6Al-4V settings, because of close melting temperature of these materials. Build area during initial experiments was kept between 700 and 750 °C. Currently sample microstructure is analyzed in order to further adjust the process parameters settings.

With as prepared powder it is possible to confirm from the micrographs (Fig. 3a) that the particle size is below 100µm with a certain fraction well below 20 µm, and particles have irregular, flaky shape. Though such powders tend to flow poorly and are not advised by the ARCAM machine manufacturers for industrial production, it was possible to use them in the modified research machine (STRC) for manufacturing test samples (Fig. 3c). Additional challenge for the EBM processing of new powders is their ability to semi-sinter. If high power e-beam hits loose powder it is charged and raises up into the working chamber ruining the build and producing risks of damaging the machine. Thus powder layers should be semi-sintered by softer beam during special preheat stage. Thus process parameter settings for new powders are adjusted for two separate stages: initial preheating and melting as such. Fig. 3b shows the start plate with complete few layers of semi-sintered powder around solid samples with 10x10 mm melt area. It should be specifically noted that precursor powder used is a composite of two different materials (MnAl and C). This is far from common in powder bed AM traditionally using only pre-alloyed powders with only few experimental studies done on the mixtures of powders [18, 19].

3. Conclusion

Different additive manufacturing techniques for magnetic materials fabrication are presented. Illustration of state-of-the-art in 3D printing of rare earth and non-rare-earth magnets, including preliminary results in production of non-rare-earth MnAl(C) permanent magnets by EBM has been shown.

Electron-beam melting of MnAl(C) magnets is an achievable task as it was explained above. Despite the not optimum process parameter settings it was possible to manufacture solid MnAl(C) samples for characterization. The future work will be focused on updating the powder compositions and optimization of EBM process parameters, aiming to reach optimal magnetic characteristics. Moreover, EBM of the rare-earth magnets is in plan.

However, the use of EBM requires quite essential additional technological tricks in order to obtain the given structure of the full-dense magnet, namely, grains of the main phase NdFeB the sizes of 0.1-10 µm separated with paramagnetic layers of Nd-rich phase, which is required for high enough coercive force of a specimen. For printed NdFeB magnets, the next goal will be an attempt of micro-texture formation by the directional crystallization. This technique will enable to enhance considerably the values of the residual magnetization, generated magnetic flow and in perspective will give chance to approach the properties of the EBM manufactured magnets to those of magnets fabricated by the commonly used sintering-based technology.

In the frame of the current work methods of stereolithographic SLA manufacturing of magnetic materials in polymer matrix are developed.

Additive manufacturing has proved to be a promising method for net-shape permanent magnets producing in order to improve magnetic properties, reduce processing costs and significantly reduce the expensive rare-earth elements waste. For bonded permanent magnets the jetting and FDM technologies are the most suitable. At the same time, for non-bonded magnets powder-based AM as SLM or EBM are the optimal solution.
Acknowledgements

This work was supported by the European Union’s Horizon 2020 NMBP23-2015 research No 686056 (NOVAMAG).

The authors would like to thank Dr. Konstantin Skokov (TU Darmstadt), Jürgen Gassmann (Fraunhofer IWKS), Shai Essel (Technion) and Dr. Alexander Katz-Demyanetz (Technion) for the advice and practical help in preparing this paper. For an access to the original data, please refer to the corresponding author.

References

[1] Additive manufacturing Magnetic Moments. 3D printers promise better, cheaper and more powerful magnets. Magnetic moments | The Economist 


