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Differential effect of magnetic alignment on additive manufacturing of magnetocaloric particles

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Abstract
Additive manufacturing of materials using magnetic particles as feedstock has attracted tremendous attention during the past decade owing to its ability to tune both shape and magnetocrystalline anisotropy, which can significantly enhance the magnetic characteristics of materials. We demonstrate that the magnetic response of multilayered thin films of Gd5Si4 can be tailored by controlling the external magnetic field during inkjet printing. The external magnetic field aligns the magnetic particles along their magnetic easy axis, enhancing the magnetic anisotropy of the printed films. Our work demonstrates the ability to print thin magnetic films with a defined anisotropy in any chosen direction with the potential to approaching magnetic properties of corresponding single crystalline materials.

Disciplines
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ABSTRACT
Additive manufacturing of materials using magnetic particles as feedstock has attracted tremendous attention during the past decade owing to its ability to tune both shape and magnetocrystalline anisotropy, which can significantly enhance the magnetic characteristics of materials. We demonstrate that the magnetic response of multilayered thin films of Gd$_5$Si$_4$ can be tailored by controlling the external magnetic field during inkjet printing. The external magnetic field aligns the magnetic particles along their magnetic easy axis, enhancing the magnetic anisotropy of the printed films. Our work demonstrates the ability to print thin magnetic films with a defined anisotropy in any chosen direction with the potential to approaching magnetic properties of corresponding single crystalline materials.

INTRODUCTION
Development of advanced magnetic materials with improved performance can be achieved through discovery of new materials, as well as by engineering microstructures of existing materials. In the latter case, there have been several reports on tuning magnetic properties by tailoring the anisotropy of nanostructured materials, including utilizing the inherent shape and crystalline anisotropy of nanoparticles, where the particles could be aligned along a specific direction by applying external magnetic field. Using additive manufacturing, the effect can be replicated in multiple layers to create functionalized materials, which can be implemented in many technological applications such as high density data storage systems, magnetic sensors, and magnetic refrigerators, to name a few.

In this study, we investigate the effect of applied external magnetic field on the deposition behavior of magnetic particles during the jetting process. Fine particles of Gd$_5$Si$_4$ magnetic particles prepared by ball-milling were formulated as ink in terpineol oil and directly deposited via magnetic field-assisted inkjet printing process onto a photopaper to generate patterned films. The particles deposit randomly on the porous substrate when printed in the absence of magnetic field. On the other hand, one-dimensional (1D) chains form along the direction of their easy axes when an external magnetic field was applied using neodymium iron boron (NdFeB) permanent magnet that was placed underneath the substrate. We show that patterns of Gd$_5$Si$_4$ fine particles have a definitive magnetocrystalline anisotropy, which can be utilized to enhance the magnetic properties through additive manufacturing for a wide range of technological and engineering applications.
EXPERIMENTAL DETAILS

Inkjet printing of magnetic particles

In this study, a photopaper (Kodak, 8.5×11” Gloss) was cut into 20 mm × 20 mm sheets and used as a porous substrate for the inkjet printing process. Briefly, Gd₅Si₄ particles were prepared by arc-melted ingot of Gd₅Si₄ via high-energy milling process. The initial coarse powder was obtained by crushing the ingot in an agate mortar and sieving to an average particles size of ~45 μm or smaller. The coarse powder was milled with poly(ethylene glycol) followed by milling in heptane to produce fine powders. Further details of the synthesis process can be found elsewhere. Then, the particles were dispersed in terpineol oil (Alpha-Terpineol, 96% purity, Alfa Aesar) to obtain ink with particle concentration of 25 mg/mL. In order to enhance the adhesion of the Gd₅Si₄ particles with the substrate, 0.15 wt% ethyl cellulose (18-22 mPa.s, 5% in Toluene + Ethanol (80:20) at 25°C, TCI America) was added to the ink. Then, the magnetic ink was ultrasonicated for 10 min before printing. The magnetic suspension was jetted on the photopaper substrate via an inkjet printer platform (Jetlab 4, MicroFab). A printing nozzle with an orifice size of 80 μm (MJ-ATP-01-80-8MX, MicroFab), was employed in this study. This piezoelectric nozzle was driven by a waveform generator (Jetdriver III, MicroFab). In order to facilitate the jetting process of terpineol oil, the nozzle was heated to 50°C. The size of the jetted droplets on the photopaper was controlled by the number of bursts, where the volume of individual jetted droplet was ~400 pl, generated at 200 Hz jetting frequency. The alignment of the magnetic particles was achieved by placing an N52 (BHmax = 52 MGOe) NdFeB permanent magnet (BC14-N52, K&J Magnetics) underneath the substrate to force the nanoparticles to align along the direction of the externally applied magnetic field. Samples with random particle orientations were printed without using the permanent magnet.

Morphology characterization

The morphology of the printed films was characterized by an ultra-high-resolution scanning electron microscope (HITACHI SU-70 FE-SEM) with 5 kV and 15 mm scanning distance. The samples were coated with platinum using a platinum sputter (Denton Vacuum Desk V) for 160 s prior to the SEM characterization.

Magnetic characterization

The magnetic properties of the printed patterns were characterized via Physical Property Measurement System (PPMS) from Quantum Design. The size of the printed films was adjusted to 4 mm × 4 mm, printed with the ink of 25 mg/mL particle concentration. Each film sample was measured in both the parallel and the normal direction of the magnetic field. To obtain the magnetic moment versus magnetic field (MH) curves, the magnetic field of the PPMS was cycled from 0 Oe to +30,000 Oe with a step rate of 100 Oe/s at temperatures ranging from 280 K to 350 K. The samples were demagnetized using demagnetization cycle after every isotherm. Magnetization vs. magnetic field (MT) measurements were recorded with temperature sweep rate of 4 K/min and used to investigate the effect of temperature on the magnetization of the deposited particles. The Curie temperature of the samples was determined as the inflection point of the Magnetothermal curve collected upon heating (i.e., as the minima of the dM/dT vs. T data). The magnetic entropy change ∆SMag, under an applied field of μ0Happ ≤ 3 T, was calculated from Maxwell’s Relation applied to M(H) isotherms measured at 5 K temperature intervals in the vicinity of the samples’ Curie temperature: ∆SMag(H, T) = μ0 ∫ H max

RESULTS AND DISCUSSION

Figure 1 is a schematic illustration of the inkjet printing process of the Gd₅Si₄ magnetic particles. As shown in Figure 2a and c, when no magnetic field is applied the particles randomly deposit on the porous substrate. However, 1D chains of magnetic particles are formed along the direction of the exerted magnetic field when a NdFeB permanent magnet is placed underneath the substrate. In order to minimize the magnetostatic energy developed in each magnetic particle, the particles orient and assemble along their easy magnetization axis (magnetization vector) parallel to the applied magnetic field vector. This in turn, combines the magnetic moment developed in each magnetic particle along the direction of the magnetic field. It is observed that the solvent slowly infiltrates the porous substrate after the printing process, leaving the printed features on top of the substrate. During this infiltration process, particularly when the magnetic field is present, the particles were found to heavily concentrate in vicinity of the substrate surface, while the top portion of sessile droplet (i.e., near the air-liquid interface) was found to be almost clear of the magnetic particles as illustrated in Figure 1. Figure 2 (a–d) shows the difference in particle deposition patterns with and without applying external magnetic field, which clearly demonstrate the 1D chain assembly of the magnetic particles.

The alignment procedure has a marked effect on the susceptibility and saturation magnetization of the aligned film. Below we will refer to the magnetically aligned film when measured with the magnetic field vector parallel to the alignment direction as “Parallel film.” The measurement with the magnetic field vector in the direction normal to the alignment of the particles will be referred as “Normal film.” The film printed without the external magnetic field is referred to as “Random film.” Figure 3 shows the hysteresis curves for Parallel, Random and Normal films measured at 300 K. From the hysteresis curve, it is evident that the magnetization and susceptibility of the aligned film reaches a maximum when measured in the direction of alignment, indicating that the alignment direction is the easy axis of the film, and the hard axis is the axis that is normal to the aligned axis. Samples with random particle orientation (no applied magnetic field during printing) exhibited magnetization less than that observed in films with 1D chains, measured along their easy axes, which definitely proves the anisotropic magnetic properties, obtained from the 1D assemblies. Inset of Figure 3 shows magnified region near the origin of the hysteresis graphs. Since, Gd₅Si₄ is a soft ferromagnetic material, the coercivity of all the 3 samples was small and nearly equal. Fig. S1 in the supplementary material shows magnetization as a function of magnetic field at room temperature of “Random film” along 3 different orientations of the film with respect to the magnetic field direction. It can be clearly noted that there is no significant variation in the magnetization indicating...
that when the external magnetic field is not used for the alignment, the film behaves like a polycrystalline sample in the parallel plane of the film.

Figure 4 presents the temperature dependent magnetization, which also shows a similar trend, where the magnetization was the highest in the easy and the lowest in the hard axes of the aligned film (Figure 4a) compared to the Random film with intermediate magnetization. All films retain the same broad transition with $|dM/dT|$ peaking at $\sim 320K$.

Figure 5 demonstrates the magnetization isotherms, obtained from 280-350K. The change in magnetic entropy $\Delta S$ was calculated from the Maxwell relation\(^8,13\), which shows entropy change with respect to temperature at applied magnetic field change of 3T. In addition, Figure 5 presents a similar behavior to that illustrated in Figure 3 and Figure 4, where Parallel film exhibit the highest $\Delta S$ followed by Random film and Normal film. All magnetic measurements, M-H, M-T and $\Delta S$ vs. T show highest magnetization and entropy for Parallel film and lowest for Normal film, which is due to the effect of both magnetocrystalline and shape anisotropy. The measured properties of the Parallel films are the highest and the lowest depending on the sample orientation with respect to the testing magnetic field; whereas, Normal films always show intermediate magnetization. Demagnetization factor was not accounted...
FIG. 4. (a) Temperature dependent magnetization data for films with aligned and random particle orientation. Parallel and Normal denote the measurement with field in the easy and the hard axis directions. (b) $dM/dT$ vs. Temperature for the Normal, Parallel and Random films showing no variation in the transition temperature.

CONCLUSION

In this study, the fine particles of Gd$_5$Si$_4$ were inkjet printed on porous substrate to examine their unique magnetic characteristics. The particles orient and form 1D assemblies along their easy axes when printing is performed under uniform magnetic field (Parallel film). In contrast, the film, fabricated in absence of applied external magnetic field, showed random distribution of particles. The 1D assembly of the magnetic particles, caused by their alignment also the easy axis, results in increased saturation magnetization, susceptibility, and magnetic entropy change in that direction. The measured magnetic properties are consistent with highly textured, single crystal-like materials, which is of significant importance for different applications. The ability to mimic single crystal-like material like properties, and the ease of control of hierarchical assembly of magnetic particles through inkjet printing provides a great potential for creating advanced material with tunable magnetic and caloric properties, which has many engineering and technological applications.

SUPPLEMENTARY MATERIAL

See supplementary material for magnetization as a function of magnetic field at room temperature of “Random film” along 3 different orientations of the film, 0°, 45° and 90° with respect to the magnetic field direction to indicate that the “Random film has same magnetization in all the directions in the parallel plane of the film.”

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