Materials and Design 118 (2017) 75–80

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Thermal and magnetic properties of nanostructured densified ferrimagnetic composites with graphene - graphite fillers

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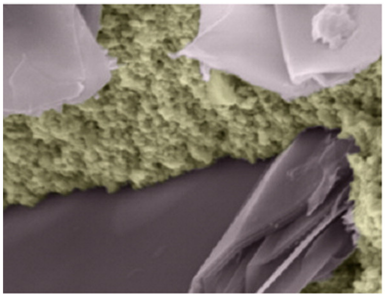
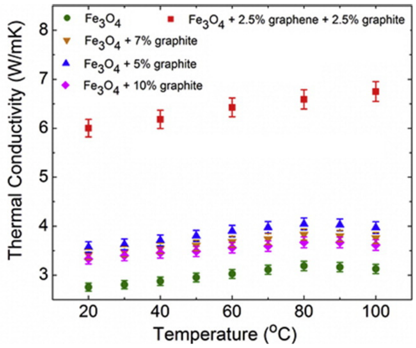
HIGHLIGHTS

- We report on synthesis of nanostructured ferrimagnetic iron oxide composites with graphene - graphite fillers for improved heat conduction in permanent magnets.
- It was demonstrated that addition of graphene and graphite fillers results in ×2.6 increase of the thermal conductivity without significant degradation of magnetization.
- Strong increase in the thermal conductivity of magnetic composites was attributed to the excellent heat conduction properties of graphene and graphite.

GRAPHICAL ABSTRACT





ARTICLE INFO

Article history:
Received 10 November 2016
Received in revised form 30 December 2016
Accepted 8 January 2017
Available online 10 January 2017

Keywords:
Permanent magnets
Graphene
Thermal conductivity
Thermal management

ABSTRACT

We report the results of an experimental study of thermal and magnetic properties of nanostructured ferrimagnetic iron oxide composites with graphene and graphite fillers synthesized via the current activated pressure assisted densification. The thermal conductivity was measured using the laser-flash and transient plane source techniques. It was demonstrated that addition of 5 wt.% of equal mixture of graphene and graphite flakes to the composite results in a factor of ×2.6 enhancement of the thermal conductivity without significant degradation of the saturation magnetization. The microscopy and spectroscopic characterization reveal that sp^2 carbon fillers preserve their crystal structure and morphology during the composite processing. The strong increase in the thermal conductivity was attributed to the excellent phonon heat conduction properties of graphene and graphite. The results are important for energy and electronic applications of the nanostructured permanent magnets.

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http://dx.doi.org/10.1016/j.matdes.2017.01.018
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1. Introduction

Magnetic nanocomposites are important for a wide range of applications, and they are playing an increasingly important role for uses in medicine [1–3], catalysis [4] and other applications [5]. The high concentration of interfaces in nanocomposites allows one to take advantage of different magnetic phases for better magnetic coupling, e.g., ferrimagnetic – antiferromagnetic, ferromagnetic – nonmagnetic. However, the operation temperature of nanostructured magnets can be severely limited owing to poor heat conduction properties of nanostructured materials, resulting in temperature rise and degradation of magnetic properties, which are highly temperature sensitive. Permanent magnets, used in a variety of applications, ranging from power sources to switches and actuators [6–7], can be exposed to temperatures higher than or approaching the Curie temperature. For this reason, thermal management of nanocomposite magnets is becoming an important consideration. The magnetization of magnetic materials decreases as the Curie point is reached. A conventional approach of avoiding it is increasing the Curie point via materials engineering and utilization of nanostructured materials [8–9]. However, another strategy – increasing the thermal conductivity, K, and thermal diffusivity, α, of permanent magnets – has not been well studied. Indeed, higher K and α would translate into lower temperature rise allowing for functioning of practical systems based on magnets with relatively low Curie temperatures. This approach may be particularly relevant to nanostructured magnets that have very low thermal conductivity owing to the heat carriers, acoustic phonons or electrons, scattering on grain boundaries and defects. An obstacle for improving heat conduction properties of nanostructured magnets is a possibility of degrading the magnetic characteristics. Thus, one should attempt to increase the thermal conductivity without substantial degradation of magnetization.

In this work, we show that the use of graphene and graphite flakes as fillers in properly synthesized nanostructured materials allows one to significantly increase the heat conduction properties of nanostructured magnets without serious degradation of their magnetization. As a model system for the proof-of-concept demonstration of our approach we used the densified nanostructured iron oxide. The bulk nanostructured samples for this study were synthesized via the current activated pressure assisted densification (CAPAD) process also known as the spark plasma sintering [10–12]. Iron oxide was chosen as a model system due to its natural abundance, ease of processing, and extensively studied properties. It is likely that the demonstrated approach of utilizing thermal fillers will work with other nanostructured magnetic materials. As an additional reference sample, we used a conventionally-sintered sample to illustrate the importance of proper steps in composite preparation for preserving magnetic properties.

As the thermal filler material we selected a mixture of graphene and graphite flakes owing to their excellent thermal properties [13–14]. High quality graphite has the in-plane thermal conductivity $K = 2000$ W/m·K at room temperature (RT). The intrinsic thermal conductivity of graphene can be even higher than that for bulk graphite basal planes [13]. Graphene and few-layer graphene (FLG) flakes were shown to work well as thermal fillers in various polymer composites used as thermal interface materials (TIMs) [15–18]. In many cases, FLG fillers perform better than graphene or graphite particles because they preserve the mechanical flexibility of graphene and do not suffer from degradation of the intrinsic heat conduction properties while in close contact with the matrix materials. However, there have been no reports of graphene, FLG or graphite thermal fillers in magnetic materials or other related mechanically hard solids. We focused our study on finding an optimum mixture of graphene and graphite fillers for nanostructured permanent magnets. Since graphene has a thickness of one atomic plane its high temperature processing with iron oxide can result in chemical reaction and alloying with a corresponding degradation of thermal properties. Graphite flake with lower surface to volume ratio are expected to be more robust for preserving their morphology and intrinsic heat conduction properties. At the same time certain fraction of graphene can be beneficial for forming heat conduction network owing to graphene flexibility and excellent coupling to matrix materials. The latter was observed in the epoxy-based TIMs where mixtures of graphene and FLG or graphene and graphite performed the best [15–17]. The cost considerations also favor the use of graphite – FLG mixtures rather than pure graphene or FLG solutions obtained by the liquid phase exfoliation or graphene oxide reduction.

2. Material synthesis

In order to synthesize the samples, we used commercial 20-nm grain size γ-Fe_2O_3 powder (Inframat Advanced Materials) and graphite (Asbury Carbons). The materials were dispersed into ethanol and then ultra-sonicated for 1 h. The ethanol was evaporated for 12 h at 80 °C and collected. In the CAPAD process the powder was rapidly densified at 600 °C with an applied load of 150 MPa [10–11]. The samples with the mixture of graphite and graphene were prepared by the same approach using commercial graphene – FLG solution (Graphene Supermarket). For comparison, we prepared several samples using traditional sintering without densification. The morphology and crystal structure of the samples were studied using scanning electron microscopy (SEM), Raman spectroscopy (Renishaw) and X-ray diffraction (XRD). Fig. 1 (a–b) shows SEM image of fracture surface of a representative ferrimagnetic iron oxide composites with graphite and graphene fillers at two distinct magnifications. Analysis of the microscopy data indicate that the samples consist of iron oxide grains and separate graphite flakes (50–800 μm diameters, 1–150 μm thick) together with graphene flakes of various lateral dimensions. The microcopy data do not show obvious signs of reaction between the iron oxide grains and graphite flakes, i.e. the CAPAD process preserved morphology.

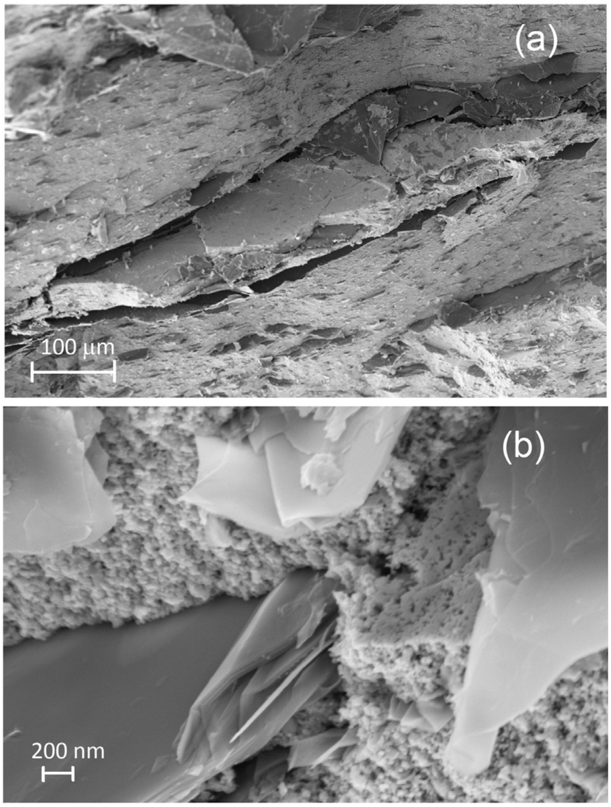

Fig. 1. (a–b): Scanning electron microscopy micrograph of nanostructured iron oxide – graphite – graphene composite at two magnifications. Note the separation of the sp^2 carbon fillers and iron oxide grains indicating that no chemical reaction happened during the composite processing. The samples were prepared using CAPAD method.