High-Temperature First-Order-Reversal-Curve (FORC) Study of Magnetic Nanoparticle Based Nanocomposite Materials

B. Dodrill[*], P. Ohodnicki[**], A. Leary[***], M. McHenry[***]

[*]Lake Shore Cryotronics, Inc.
575 McCorkle Blvd., Westerville, OH, USA, brad.dodrill@lakeshore.com
[**]National Energy Technology Lab, Pittsburgh, PA, USA, paul.ohodnicki@netl.doe.gov
[***]Carnegie Mellon University, Materials Science and Engineering, Pittsburgh, PA, USA,
aleary@andrew.cmu.edu, mm7g@andrew.cmu.edu

ABSTRACT

First-order-reversal-curves (FORCs) are an elegant, nondestructive tool for characterizing the magnetic properties of materials comprising fine (micron- or nano-scale) magnetic particles. FORC measurements and analysis have long been the standard protocol used by geophysicists and earth and planetary scientists investigating the magnetic properties of rocks, soils, and sediments. FORC can distinguish between single-domain, multi-domain, and pseudo single-domain behavior, and it can distinguish between different magnetic mineral species [1]. More recently, FORC has been applied to a wider array of magnetic material systems because it yields information regarding magnetic interactions and coercivity distributions that cannot be obtained from major hysteresis loop measurements alone. In this paper, we will discuss this technique and present high-temperature FORC results for two magnetic nanoparticle materials: CoFe nanoparticles dispersed in a SiO_2 matrix, and FeCo-based nanocrystalline amorphous/nanocomposites.

Keywords: magnetometry, first-order-reversal-curves, FORC, nanoscale magnetic materials

1 FIRST-ORDER-REVERSAL-CURVES (FORC)

The most common measurement that is performed to characterize a material's magnetic properties is measurement of the major hysteresis loop M(H). The parameters that are most commonly extracted from the M(H) loop are: the saturation magnetization M_s, the remanence M_r, and the coercivity H_c.

First-order-reversal-curves (FORCs) [2] can give information that is not possible to obtain from the hysteresis loop alone. These curves include the distribution of switching and interaction fields, and identification of multiple phases in composite or hybrid materials containing more than one phase [3,4]. A FORC is measured by saturating a sample in a field H_{sat}, decreasing the field to a reversal field H_a, then measuring moment versus field H_b as the field is swept back to H_{sat}. This process is repeated for many values of H_a, yielding a series of FORCs. The measured magnetization at each step as a function of H_a and H_b gives $M(H_a, H_b)$, which is then plotted as a function of H_a and H_b in field space. The FORC distribution $\rho(H_a, H_b)$ is the mixed second derivative, i.e., $\rho(H_a, H_b) = -(1/2)\partial^2 M(H_a, H_b)/\partial H_a \partial H_b$.

The FORC diagram is a 2D or 3D contour plot of $\rho(H_a, H_b)$. It is common to change the coordinates from (H_a, H_b) to $H_c = (H_b - H_a)/2$ and $H_u = (H_b + H_a)/2$. H_u represents the distribution of interaction or reversal fields, and H_c represents the distribution of switching or coercive fields.

2 HIGH-TEMPERATURE FORC RESULTS FOR NANOPARTICLE BASED NANOCOMPOSITE MAGNETIC MATERIALS

To demonstrate the utility of the FORC measurement and analysis protocol for characterizing high-temperature magnetic properties of materials, measurements were conducted for two different magnetic nanoparticle materials: CoFe nanoparticles dispersed in a SiO_2 matrix [5], and both as-cast and crystallized FeCo-based nanocrystalline amorphous/nanocomposites [6]. All magnetic measurements were performed using a Lake Shore Cryotronics MicroMag™ vibrating sample magnetometer (VSM) with a high-temperature furnace, enabling variable temperature measurements from room temperature to 800 °C. All measured magnetization data are presented in terms of the magnetic moment (emu) as a function of field (Oe) and temperature (°C). There are a number of open source FORC analysis software packages such as FORCinel [7] and VARIFORC [8]. In this paper, custom analysis software was used to calculate the FORC distributions and plot the FORC diagrams.

2.1 CoFe Nanoparticles Dispersed in an SiO_2 Matrix

The hysteresis M(H) loops and FORCs were measured at temperatures of T = 25, 100, 200, 300, and 400 °C for a sample containing 40% volume fraction of CoFe nanoparticles dispersed in a 60% volume fraction of SiO_2.

Transmission electron microscope (TEM) images show that the CoFe nanoparticles are approximately 10 nm in diameter and separated by an intergranular SiO_2 phase [5]. Figure 1 shows the hysteresis loops at each temperature and shows that the coercivity H_c decreases with increasing temperature. Figure 2 shows the measured FORCs at 25 °C, and figure 3 shows the 2D FORC diagrams at temperatures ranging from 25 to 400 °C. There is a single peak in the FORC distribution at each temperature that is centered at H_c and that shifts towards lower switching fields as temperature increases, coincident with the decrease in H_c with increasing temperature. In a FORC diagram, entirely closed contours are typically considered to be a fingerprint of single-domain (SD) particles, whereas entirely open contours that diverge towards the H_u axis are a fingerprint of multi-domain (MD) behavior [1]. The results shown in figure 3 demonstrate closed contours at lower temperatures and open contours at increasing temperatures, suggesting a transition from SD to MD behavior based upon the conventional interpretation of FORC diagrams. Further studies are required to better understand if this traditional interpretation is valid for such densely packed nanoparticle aggregates. At all temperatures there is a distribution of both interaction (H_u, vertical axis) and switching fields (H_c, horizontal axis), the former owing to interparticle interactions, and the latter due to different particles switching at different applied field strengths.

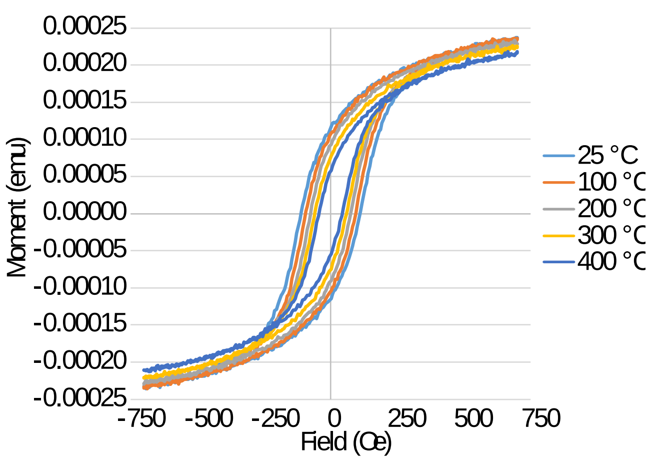

Figure 1: Hysteresis loops at T = 25, 100, 200, 300 and 400 °C.

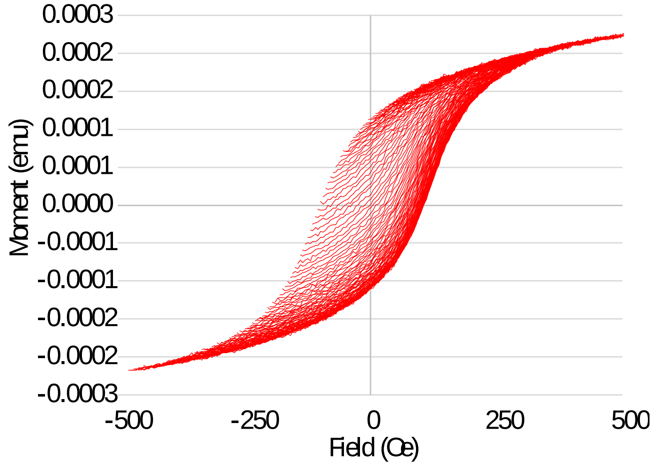

Figure 2: Measured FORCs at 25 °C.

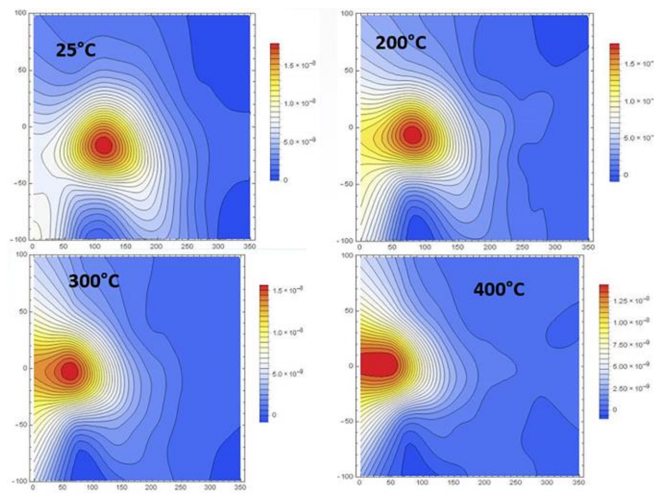

Figure 3: 2D FORC diagrams at T = 25, 200, 300 and 400 °C.

2.2 FeCo-based Nanocrystalline Amorphous/Nanocomposites

Samples were fabricated using a conventional melt spinning process, and TEM images show that the samples are fully amorphous (as-cast) or composed of nanocrystal diameters <~10 nm embedded in an intergranular amorphous phase after being subjected to a primary crystallization treatment at approximately 520 ºC ('crystallized'). The hysteresis M(H) loops and FORCs were measured for disc-shaped samples (0.3 cm diameter) with the applied field oriented parallel to the ribbon plane, and at temperatures of T = 25, 400, and 780 °C for both as-cast and crystallized specimens with the latter temperature being sufficiently high for the well-known 'secondary crystallization' process to occur resulting in crystallization of any remaining amorphous precursor. Figures 4 and 5 show the M(H) loops at each temperature and the measured FORCs at 780 °C for

 TechConnect Briefs 2016, TechConnect.org, ISBN 978-0-9975-1170-3

both initially as-cast and crystallized specimens, respectively. Figure 6 shows the 2D FORC diagrams for as-cast (top) and crystallized (bottom) samples at T = 25 , 400 and 780 ° C . These diagrams show a wishbone-like feature that is often seen in FORC diagrams. Wishbone FORCs typically mean that there are dipolar (or magnetostatic) interactions between particles. Because the Curie temperature of the amorphous phase is approximately 520 °C, at elevated temperatures dipolar interactions could indeed become an important interaction, whereas at lower temperatures the nanoparticles and amorphous precusor should be fully exchange coupled. The peak in the FORC distribution is shifted towards positive reversal or interaction fields (H_u, vertical axis) for both samples as temperature increases, which can suggest that dipolar interactions are becoming increasingly important with increasing temperature near and above the Curie temperature of the amorphous precursors.

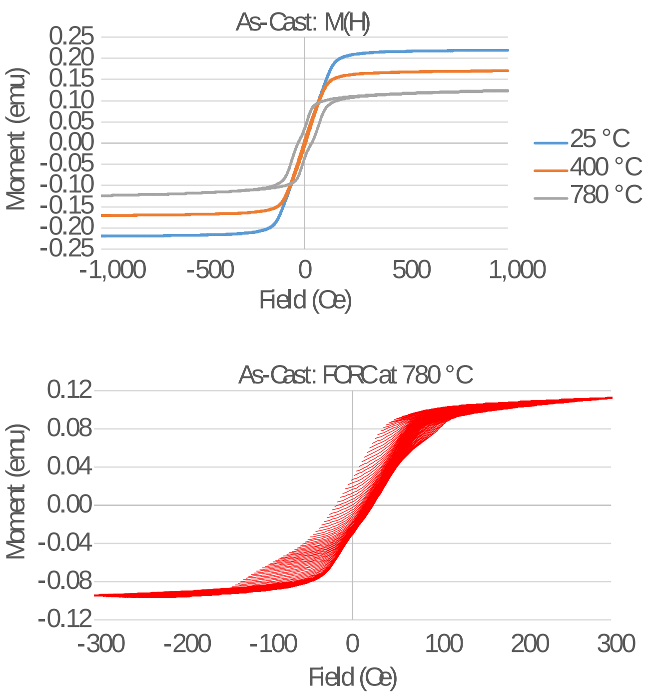

Figure 4: M(H) at 25, 400 and 780 °C, and the measured FORCs at 780 °C for a as-cast FeCo-based nanocrystalline amorphous/nanocomposite sample.

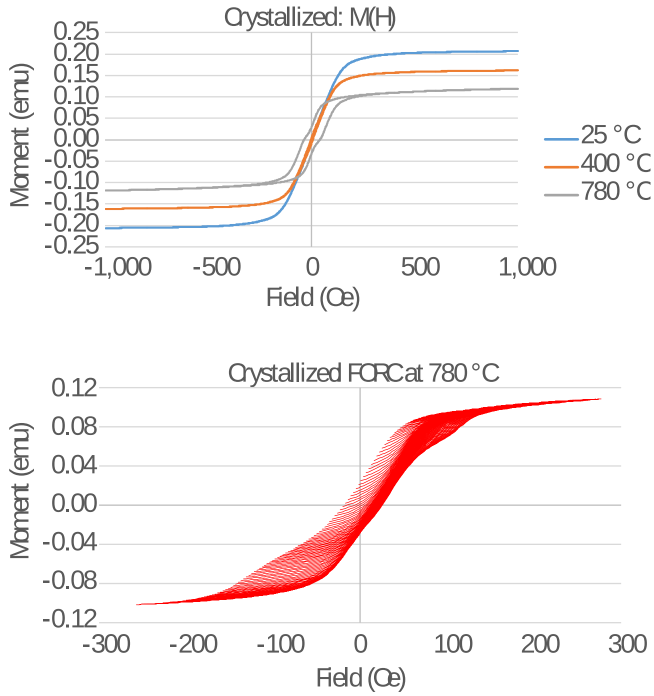

Figure 5: M(H) at 25, 400 and 780 °C, and the measured FORCs at 780 °C for a crystallized FeCo-based nanocrystalline amorphous/nanocomposite sample.

3 CONCLUSIONS

FORC analysis is indispensable for characterizing interactions and coercivity distributions in a wide array of magnetic materials, including; natural magnets, nanowire arrays [9], permanent magnets [10], and exchanged coupled magnetic multilayers [11]. In this paper, we have shown the evolution at high temperatures of the distribution of switching and interaction fields as determined from FORC analysis for CoFe nanoparticles and FeCo-based nanocrystalline magnetic materials.

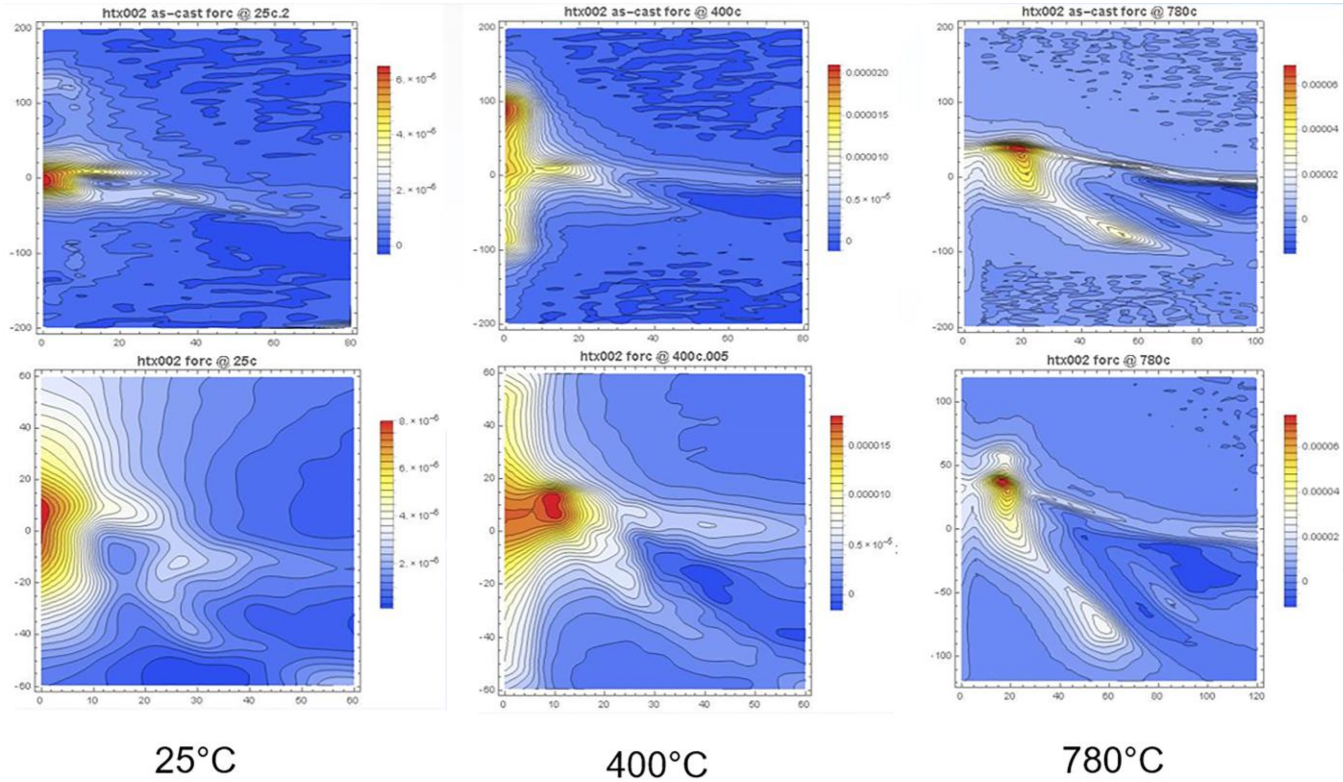

Figure 6: 2D FORC diagrams at 25, 400 and 780 °C for initially as-cast (top) and crystallized (bottom) FeCo-based nanocrystalline amorphous/nanocomposites.

REFERENCES

[1] A.R. Muxworthy, A.P. Roberts, First-order-reversal-curve (FORC) diagrams, Encyclopedia of Geomagnetism and Paleomagnetism. (Spring, 2007).

[2] C.R. Pike, A.P. Roberts, K.L. Verosub, Characterizing interactions in fine particle systems using first order reversal curves, Journal of Applied Physics. 85 6660 (1999).

[3] B.C. Dodrill, First-order-reversal-curve analysis of multi-phase ferrite magnets, Magnetics Business and Technology. (Spring 2015).

[4] C. Carvallo, A.R. Muxworthy, D.J. Dunlop, First-order-reversal-curve (FORC) diagrams of magnetic mixtures: Micromagnetic models and measurements, Physics of the Earth and Planetary Interiors. **154** 308 (2006).

[5] P. R. Ohodnicki, Jr. V. Sokalski, J. Baltrus, J. B. Kortright, X. Zuo, S. Shen, V. Degeorge, M. E. McHenry, D. E. Laughlin, Structure-Property Correlations in CoFe-SiO_2 Nanogranular Films Utilizing X-ray Photoelectron Spectroscopy and Small-Angle Scattering Techniques, Journal of Electronic Materials 43 (1), 142–150 (2014).

[6] S. Shen, P. R. Ohodnicki, S. J. Kernion, A. M. Leary, V. keylin, J. F. Huth, M. E. McHenry, Nanocomposite Alloy Design for High Frequency Power Conversion Applications, https://www.researchgate.net/publication/236174216_Nanocomposite_Alloy_Design_for_High_Frequency_Power_Conversion_Applications.

[7] R.J. Harrison, J.M. Feinberg, FORCinel: An improved algorithm for calculating first-order reversal curve distributions using locally weighted regression smoothing, Geochemistry, Geophysics, Geosystems. **9** 11 (2008). FORCinel may be downloaded from: https://wserv4.esc.cam.ac.uk/nanopaleomag/?page_id=31.

[8] R. Egli, VARIFORC: An optimized protocol for calculating non-regular first-order reversal curve (FORC) diagrams, Global and Planetary Change. (2013). p. 110, 203.

[9] B. C. Dodrill, L. Spinu, First-order-reversal-curve analysis of nanoscale magnetic materials, *Technical* Proceedings of the 2014 NSTI Nanotechnology Conference and Expo, CRC Press (2014).

[10] B. C. Dodrill, First-order-reversal-curve analysis of nanocomposite permanent magnets, Technical Proceedings of the 2015 TechConnect World Innovation Conference and Expo, CRC Press (2015).

[11] B. C. Dodrill, Magnetometry and First-Order-Reversal-Curve (FORC) Studies of Nanomagnetic Materials, Dekker Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis (2016).