

Induction heating of FeCo nanoparticles for rapid rf curing of epoxy composites

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FeCo magnetic nanoparticles (MNPs) have been investigated for curing polymer epoxy composites through radio-frequency (rf) heating. The rf response of functionalized FeCo MNPs is shown to uniformly cure the epoxy without parasitic heating for potential applications in electronic packaging. The FeCo/(Co,Fe)₃O₄ MNPs were synthesized using a rf induction plasma torch and were ultrasonicated in diglycidyl ether of bisphenol F epoxy to form stable ferrofluids. Transmission electron microscopy studies reveal as-synthesized MNPs to have a mean diameter of 17.6 nm with a 5.2 nm standard deviation. The mean MNP diameter is reduced to 9 nm after cryomilling and causes particles to form ~200 nm agglomerates. Ferrofluids of varying MNP concentrations, sizes, and shapes were rf heated using a precision rf coil operated at 20.0 kA/m and 267 kHz frequency. Using a 1.36 vol % ferrofluid, the epoxy composite was effectively rf cured, reaching temperatures >100 °C in ~70 s. The results suggest that rf heating of FeCo MNPs may provide an effective method to curing epoxy composites. © 2009 American Institute of Physics.

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I. INTRODUCTION

Functionalized magnetic nanoparticles (MNPs) and derived fluids hold significant promise for many radio-frequency (rf) heating applications. These applications include hyperthermia and thermoablative cancer therapies,^{1,2} selective heating of nanoparticles for catalysts in synthesis reactions, and rf curing of polymers/epoxies. Crucial to many such applications is the synthesis of MNPs with appropriate magnetic properties, functionalization of the nanoparticles, dispersion of nanoparticles into fluids, and determination of the efficacy of rf heating.

When an alternating magnetic field is applied, magnetic materials are observed to heat as a result of losses occurring due to the internal rotation of the magnetization and rotation of the MNP in a viscous medium. Rosensweig's theory³ predicts the size dependence of the MNP heat dissipation by Néel and Brownian relaxation in response to a rf field. The magnetic heating rate depends on extrinsic properties such as viscosity of the fluid, particle size, and distribution, as well as intrinsic material properties such as saturation magnetization and magnetic anisotropy energy density.

In this paper we address the rf heating of MNPs for curing the epoxy underfill layer used in flip-chip semiconductor packaging technology. In the flip-chip packaging process, a low viscosity epoxy underfill material is applied between the silicon chip and substrate layers (see Fig. 1), which protects the chip face against moisture and tempera-

ture variations as well as provides for a mechanically stronger structure.⁴ Typically, the entire package is placed in an oven to cure this underfill epoxy. This thermal cycling of the package leads to nonuniform temperature distributions in the epoxy, which can cause polymer shrinkage, delaminating, and cracking of the polymer. An alternative curing process involves remote, noncontact rf heating of MNP loaded epoxies, which allow for uniformly curing the epoxy at room temperature without parasitic heating effects to the rest of the package.

This paper addresses the use of FeCo/(Co,Fe)₃O₄ MNPs to uniformly cure the epoxy underfill layer used in flip-chip technology. FeCo/(Co,Fe)₃O₄ MNPs have advantages over iron oxide particles (Fe₃O₄), typically used in rf curing applications, due to having the highest saturation magnetization, which results in a larger heating rate,² and form stable, protective ferrite shells,⁵ which aid in their func-

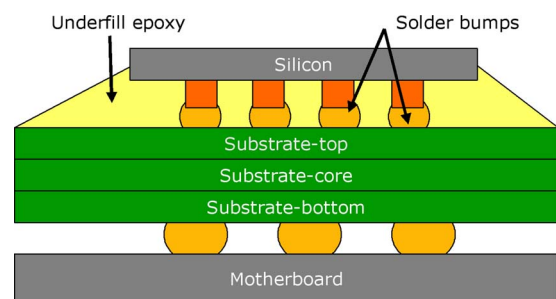


FIG. 1. (Color online) Schematic of the underfill epoxy layer in the flip-chip processing technique.

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tionalization and prevents corrosion and degradation of magnetic properties. The ionic oxide layer also enhances the attachment to certain polymer surfactants, which enable functionalization and the production of a stable FeCo ferrofluid.

II. EXPERIMENTAL PROCEDURE

Polydisperse FeCo nanoparticles of composition Fe₅₀Co₅₀ were synthesized using a 50 kW, 4 MHz rf Tekna induction plasma torch (PT). We have previously described the production of graphite-coated FeCo nanoparticles by PT synthesis^{6,7} starting with a mixture of Fe–Co metal precursors. For synthesis of oxide-coated particles, we start with a 50:50 Fe to Co with 1%–2% Nb and V alloy precursor powders produced by gas atomization,⁸ sieved using a –500 mesh, and then operate the PT in air. The plasma power was kept at 42 kW while an Ar plasma gas was flowing at 86.6 slpm (standard liters per minute) surrounded by a sheath gas consisting of 55.1 slpm of Ar mixed with 9.4 slpm of hydrogen. The pressure in the reactor was maintained at 300 Torr during the synthesis. Consistent with previous experience,⁵ the resulting FeCo MNPs had a thin adherent (Fe,Co)-ferrite shell.

To achieve smaller particles than as-PT synthesized powders, mechanical milling was employed. High energy mechanical milling at cryogenic temperatures was used in an attempt to decrease the particle size before incorporating them into a ferrofluid. The size and shape of the cryomilled nanoparticles were characterized using JEOL 2000EX transmission electron microscopy (TEM). Using both selected area electron diffraction and x-ray diffraction, the nanoparticles were shown to be composed of metallic FeCo in the bcc phase. dc magnetic properties of the nanopowder were studied using a Lakeshore vibrating sample magnetometer and showed similar saturation magnetization values to the as-PT powders.

The as-PT synthesized and cryomilled nanoparticles were incorporated into diglycidyl ether of bisphenol F (DGEBF) resin to form stable ferrofluids. Bisphenol F was chosen as an ideal candidate for the underfill epoxy due to its low viscosity, mechanical integrity, chemical makeup, and a high degree of cure at ambient temperatures. FeCo ferrofluids were prepared on the basis of vol % nanoparticles in solution. A constant 10 ml volume of DGEBF resin was added to different vol % of FeCo MNPs to synthesize ferrofluid solutions ranging from 0.5 to 3.0 vol %. The solutions were ultrasonicated to encourage dispersion of the particles by breaking up aggregates formed due to magnetostatic forces. Ferrofluids remained stable for several weeks.

Heating of the MNP loaded epoxies was performed using an Ameritherm Hotshot 2.0 kW rf power supply. This unit has a variable frequency between 150 and 400 kHz with a maximum output of 300 A through a three-turn coil. Applying a 20.0 kA/m ac magnetic field at 267 kHz, temperature change was measured as a function of exposure time in the as-PT and cryomilled FeCo ferrofluids using a Luxtron optical fiber temperature probe. Heating rates for concentra-

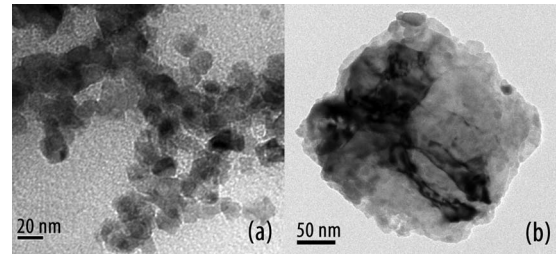


FIG. 2. (a) Typical TEM micrograph of FeCo particles from PT synthesis. (b) As-PT synthesized FeCo particles after 4 h of mechanical milling at cryogenic temperatures.

tions of 1.36 and 2.72 vol % ferrofluids with as-PT and cryomilled FeCo nanoparticles were measured.

III. RESULTS AND DISCUSSION

Initial particle size, size distribution, and structural characterization of the as-PT FeCo nanopowder were determined by TEM [Fig. 2(a)]. Synthesized nanoparticles had a mean diameter of 17.6 nm with a 5.2 nm standard deviation, as determined by measuring a 121 particle sample. Figure 2(b) shows a typical TEM image of the cryomilled particles, with an average diameter of 9 nm and a much smaller particle size distribution. Despite the particles being of smaller size, the cryomilling process causes particles to agglomerate into a 200 nm structure.

The rf heating response of the two different synthesis routes for FeCo MNPs loaded into DGEBF resin was studied. Figure 3 shows the heating rates for 1.36 and 2.72 vol % concentrations of the as-PT powders as compared to the 1.36 vol % cryomilled concentration in 10 ml solutions of DGEBF. Three 10 ml solutions of each individual sample were used in order to show any variability in the measurements (shown as error bars in Fig. 3).

The cryomilled MNPs consistently showed the largest heating rate, reaching epoxy curing temperatures of >100 °C in ~70 s. This curve shows an exponential increase in temperature with time before reaching the curing point of the DGEBF solution. Using the FeCo cryomilled

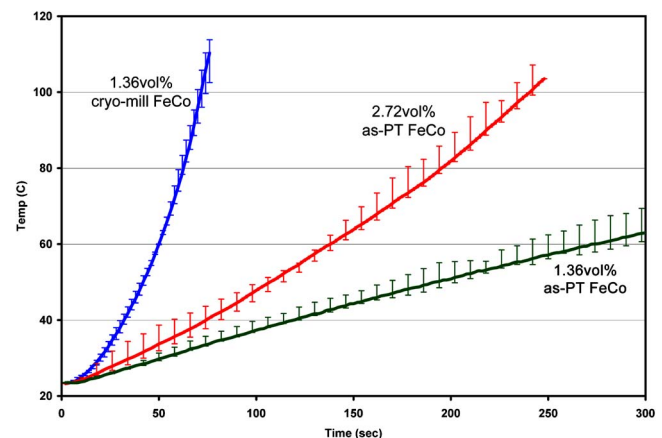


FIG. 3. (Color online) Heating curves for given concentrations of the different synthesis methods for FeCo MNPs in 10 ml DGEBF. Error bars show variability between three solutions of the sample. rf coil operating at a field amplitude of 20.0 kA/m and a frequency of 267 kHz.

nanoparticles, much higher temperatures are achievable in relatively short rf excitation times, allowing for application in the efficient curing of epoxies with higher curing points.

The large difference in heating rate between the cryomilled particles and the as-PT particles can be explained by particle size effects. According to Habib's extension of the Rosensweig model for rf heating of FeCo ferrofluids,^{2,3} larger peak heating rates are expected for more monodisperse solutions and at particle sizes smaller than the average diameter of the as-PT synthesized FeCo powder (depending on magnetic anisotropy of the material). Near the Fe₅₀Co₅₀ composition, the magnetocrystalline anisotropy is small, and therefore the peak heating rate is expected to occur at larger particle sizes. However, the role of interfacial anisotropy due to the exchange bias coupling between the FeCo core and ferrite shell is not accounted for in considering only magnetocrystalline anisotropy.

With cryomilling we expect both the size and interfacial anisotropy to change. The narrowing of the particle size distribution increases the peak heating rate. In addition, the interfacial anisotropy will shift the peak heating rate to smaller particle diameters. The combined effect can lead to a significant shift in the observed heating rates. An interfacial contribution to the magnetic anisotropy is expected for the agglomerated 9 nm particles. The size reduction and interfacial anisotropy effects from cryomilling are therefore consistent with a higher heating rate than for the as-PT particles. Modeling of these particle effects is of current interest to our research group and is presented by Sawyer *et al.*⁹

IV. CONCLUSION

Novel FeCo/epoxy nanocomposites have been produced through the incorporation of as-PT and cryomilled nanoparticles in DGEBF. The nanoparticle additives were shown to uniformly cure the epoxy underfill layer, reaching temperatures of >100 °C in ~70 s using the proposed noncontact heating process. This room temperature assembly method has the possibility of eliminating the thermal cycling of the silicon and increasing die lifetimes.

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