



Structural characterization and microwave properties of chemically functionalized iron particles obtained by high-energy ball milling in paraffin-containing organic environment



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ABSTRACT

Magnetodielectric composites comprising dispersed metal particles as magnetic filler and organic dielectrics as a host matrix are of great importance because of both technological and fundamental interests. Surfactant-assisted high-energy ball milling in organic media is successfully used for the dispersion and surface modification of metal particles. In this paper, we have carried out structural and chemical characterization of iron particles (bulk/surface) prepared in paraffin-containing environment. The study was performed with high-resolution X-ray spectroscopic techniques using synchrotron radiation from BESSY II/HZB Berlin and DORIS/DESY Hamburg. It has been shown that high-energy ball milling leads to nanofragmentation of iron grains and formation of bare metal surface which is very active in dehydrogenation of organic molecules. The paraffin molecules are destructed with the accumulation of polycondensed aromatic structures containing covalently-bound paraffin residues on the iron surface. Under dry milling (without solvent), the organic environment molecules decompose almost completely, while under wet milling, the destruction of paraffin and perfluorononanoic acid molecules slows down significantly. An addition of perfluorononanoic acid along with n-heptane into the milling liquid results in sharp change in microwave characteristics, which may be attributed to formation of platelet-shaped particles with the surface covered with long-chain residues of paraffin and surfactant molecules.

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1. Introduction

Magnetodielectric composites comprising dispersed metal particles or clusters as magnetic fillers and organic dielectrics as a host matrix are of great importance because of both technological and fundamental interests. Magnetodielectrics are successfully used in many practical applications including microwave absorbing materials [1–3]. Besides their useful applications, such materials give opportunity for studying metal/organic interactions. One of the main techniques used for the successful dispersion of metal particles in various organic matrices providing an appropriate chemical compatibility is their joint high-energy mechanical milling [4]. Surfactants added into milling liquids adsorb on the surface of powder particles, preventing their agglomeration and cold welding and facilitating their fracturing [5]. High-energy milling in the presence of surfactants results in platelet particles [6,7] needed for tailoring required magnetic properties. Furthermore, the layers of surfactant molecules may prevent oxidation of powder particles. Such magnetic particles can be used as efficient fillers for the fabrication of various functional composites.

Recently, magnetodielectric Fe/paraffin composites were fabricated by single-stage high-energy mechanical milling of Fe powder in paraffin [8] and proved to be efficient microwave absorbers. However, it has been found from the measurement of permittivity that the as-synthesized composites are conductive even if the concentration of the metal filler is less than 20 vol.%, that is significantly below the percolation threshold (~37 vol.%). It might be explained by the formation of molecular structures in an organic matrix under mechanochemical synthesis, which may serve as traps of charge carriers. Changes occurring in the metal/paraffin interface require careful analysis of the interface structural state, involving a variety of different methods, including surface-sensitive ones.

An approach suggested in this study is the fabrication of chemically functionalized metal particles with the use of surfactant-assisted high-energy ball milling. Paraffin is used as the main component of the milling environment because of its reasonable dielectric properties, chemical inertness and good technological properties [9]. However, the chemical inertness of paraffin may result in poor adhesion between metal and matrix giving rise to numerous defects, including pores, voids and gasses at the metal/organic interface, which might impair the functional properties of the composites. The processes of interaction between paraffin and metal, in particular under high-energy ball milling, are far from being comprehensively understood.

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The aims of this work were (i) to fabricate magnetic filler particles by means of the surfactant-assisted ball milling of Fe powder in paraffin; (ii) to carry out thorough structural characterization of the as-fabricated metal particles with X-ray diffraction (XRD), Mössbauer spectroscopy, and X-ray absorption spectroscopy including XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) regions of the measured Fe K edge X-ray absorption spectra; (iii) to perform detailed analysis of the organic layers formed on metal particle surface and substances of milling environments by means of Fourier-Transform Infrared (FT-IR) spectroscopy, Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) as well as XANES spectroscopy at the carbon K edge; (iv) to investigate the effect of surfactant and solvent addition to the milling environment on microwave performance of magnetodielectric composites fabricated from the synthesized filler particles.

2. Material and methods

2.1. Materials and sample preparation

Fe/paraffin composites were prepared by high-energy mechanical milling of Fe powder (99.98%) with paraffin in the ratio of 80:20 vol.%. The starting Fe powder particles had a spherical shape, with the size of less than 5 μm . Mechanical milling was carried out in a Fritsch P7 planetary ball mill. Vials and balls (16 pcs, $D = 12$ mm) were made of the hardened steel containing 1.0% C and 1.5% Cr. The sum weight of Fe and paraffin loaded into a vial was 10 g. The duration of milling was 24 h. The procedure was conducted in two different regimes. In the first regime, paraffin was preliminarily dissolved in the heated distilled heptane (20 g), while in the second regime paraffin was used in its initial solid state. It should be noted that even for the dry regime, paraffin was in the molten state during the mechanical milling, since this process is accompanied by mechanically stimulated heating of vials and balls. The temperature of the vial walls did not exceed 60 °C due to the forced air-cooling. Perfluorononanoic acid (PFNA) in the amount of 0.6 g was added as a surfactant if that was the case and the corresponding samples are denoted as *FD* and *FW* for dry and wet milling, respectively. The samples milled with no surfactant are designated as *ND* and *NW* for dry and wet milling, respectively.

After milling, the vials were cooled to room temperature and the powder was separated from the milling environment by decantation. Then the precipitate was boiled for 1 min in 10 ml of the distilled petroleum ether and ultrasonicated for 1 min. This procedure was repeated five times. After that, the sample powders with the ether were placed in a container, blown dry with argon, kept for several days in argon-filled containers until the characterization.

2.2. Techniques and instrumentation

2.2.1. Secondary electron microscopy (SEM)

The morphology of the particles was characterized by scanning electron microscopy (SEM) with the use of LEO 982FE-SEM microscope. The samples for microscopic study were prepared using the procedure described above in the [Materials and sample preparation](#) section. After dissolving the matrix the powders were deposited on a glass substrate and dried.

2.2.2. X-ray diffraction (XRD) and Mössbauer spectroscopy

The crystallographic structure of metal particles was identified by X-ray diffraction (XRD) at a DRON-3 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). Qualitative and quantitative X-ray diffraction analysis was performed using the software package [10].

The Mössbauer spectra were measured at room temperature with a YaGRS-4M spectrometer in the constant acceleration mode with ^{57}Co source embedded in the Cr matrix. The spectra were mathematically treated using the generalized regular algorithm for solving ill-posed

problems in order to obtain the hyperfine magnetic field distribution functions $P(H)$. The algorithm is described in detail elsewhere [11].

2.2.3. X-ray absorption spectroscopies (XAS)

XAS is a powerful tool for detailed structural investigations of the mechanically milled nanocrystalline materials, which do not present long-range order. The XAS technique is sensitive to the local structure up to 5–10 Å around an absorbing atom. In the XAS experiment, the absorption intensity is registered as a function of the incident photon energy tuned by means of synchrotron radiation. XAS is divided into two techniques: X-ray Absorption Near-Edge Structure (XANES) considering strong oscillations appearing just beyond the absorption edge threshold (~50 eV) and attributed to transitions to localized electronic states, and Extended X-ray Absorption Fine Structure (EXAFS) analyzing the pronounced periodic structures observed above the absorption edge due to the interference between the outgoing photoelectron wave and the wave backscattered from the nearest neighbor atoms [12,13]. It should be noted that the term XANES is typically used for hard X-ray absorption spectra, while for the soft X-ray spectra region the term NEXAFS (Near-Edge X-ray Absorption Fine Structure) is applied [14]; in physical essence the terms are interchangeable. So, hereafter we will use the same term XANES to describe both Fe K and C K edges regions in order not to confuse the discussion. XANES oscillations can be explained in terms of multiple scattering of photoelectrons by the local atomic environment of the absorbing atom and are capable of giving information on the oxidation state and local geometry coordination of the absorbing atom, while EXAFS is used to determine the distances, coordination number, and species of neighboring atoms around the absorbing one. EXAFS oscillations can be considered as the sum of sine waves, each arising from a shell of neighbors of a particular type of atom at a certain radius from the absorbing atom. The intensity of the oscillations will depend on the type and the number of backscattering atoms.

X-ray absorption spectra at the Fe K edge (7112 eV) were collected at the DORIS III synchrotron radiation storage ring at the HASYLAB/DESY, beamline A1, using a Si(111) double crystal monochromator. To increase surface sensitivity we used not only conventional transmission geometry to record the X-ray absorption spectra of the samples, but also the total electron yield (TEY) detection, thus taking advantage of the limited sampling depth of this technique (~20 nm). In the transmission mode, the spectra were acquired using ion chambers filled with argon. For the energy calibration a Fe foil was measured simultaneously using a third ionization chamber. The samples for the transmission measurements were prepared as pellets (13 mm dia.) hydraulically pressed from the calculated amount of the powder thoroughly mixed and ground with cornstarch as a diluent.

For the TEY experiments, the samples were prepared by fixing powders on a carbon tape. The reference spectra of model compounds (mechanically milled Fe powder; iron oxides) were measured in the conventional transmission mode. The number of spectra averaged for each sample varied from three to five to obtain spectra of adequate quality. Both EXAFS and XANES regions of the X-ray absorption spectra of the Fe K edge were measured and analyzed.

The experimental XAS spectra were calibrated and background-subtracted using a smooth cubic-spline function to fit the atomic-like background above the absorption edge. The near-edge background-subtracted spectra were normalized to the absorption step height by fitting the pre-edge and post-edge background.

The EXAFS data analysis was performed according to the conventional procedure by applying an IFEFFIT code [15]. It involved the following steps: (a) the EXAFS signal was extracted by subtraction of a function of atomic absorption; (b) the derived EXAFS signal was converted from the energy space into the wave number space k ($\chi(k)$); (c) a weight factor of k^3 was applied to $\chi(k)$ to compensate the oscillation attenuation effect; (d) the k^3 -weighted EXAFS signal was Fourier transformed in the region of 3–14 Å⁻¹. The modulus of the Fourier

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