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Structural Study of a Composite Material Based on Ultra-High Molecular Weight Polyethylene and Mechanochemically Synthesized Magnesium Ferrite

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Abstract

The structural and morphological characteristics of mechanochemically synthesized highly dispersed magnesium ferrite are studied. The change of structural characteristics of ultra-high molecular weight polyethylene (UHMWP) during mechanical activation is investigated. The structural characteristics of mechanochemically synthesized composite material UHMWP/magnesium ferrite, as a precursor to create materials for protection against electromagnetic radiation, are studied by means of scanning electron microscopy, X-ray diffraction and differential scanning calorimetry.

Keywords: mechanical activation, mechanocomposites, mechanochemical synthesis, ultra-high molecular weight polyethylene, magnesium ferrite

INTRODUCTION

Protection of electronic equipment, machinery and humans from electromagnetic and ionizing radiation remains an urgent problem [1, 2], so the search for relevant materials requires new and simple solutions. At present, several approaches are proposed to obtain light and easily moldable protective materials. One of these approaches is the use of polymer composite materials [3] in which the individual absorbing capacities of polymers and modifying agents are involved. The comparable size of modifying particles and radiation wavelength allows varying the effective beam path length in the composite material due to the effects of additional absorption and scattering of the radiation.

The mechanisms of protection from ionizing radiation include multiple reflections (from different surfaces and interfaces). For the formation of the composite based on a polymer, the capacity of metals and their compounds to absorb a specific kind of radiation is taken into account, while the use of a modifying agent in the form of ultrafine particles in combination with a polymeric matrix may provide the light weight and moldability of the material [4]. Ferrites as the components of composite materials attract attention because of their electromagnetic properties [5, 6] and are used to make coatings protecting from electromagnetic radiation, in particular for individual protection of portable devices and humans [7].

The properties of ferrites are strongly dependent on the structure, morphology and size of par-

ticles [8], so the practical application of materials based on them requires the control of these parameters during the synthesis. The uniform distribution of particles in the polymer, strong interfacial binding are the most important tasks for obtaining the composite materials. The main methods of the synthesis of ferrites are well developed at present [9]. However, the search for new factors affecting the uniformity of phase composition, structural perfection, granulometric uniformity, reproducibility of characteristics, decrease in economic expenses is still carried out.

We chose the components for the model composite: magnesium ferrite (MgFe_2O_4) as one of the most widespread compositions used in electronics, catalysis, sensor technologies [10–12], and ultra-high molecular weight polyethylene (UHMWP) which exhibits high mechanical characteristics and chemical stability against aggressive media when used as a matrix and binder in composite materials [13].

The synthesis of MgFe_2O_4 using known chemical methods (co-precipitation, sol-gel, hydrothermal method) is investigated rather thoroughly and allows obtaining the particles of uniform granulometric and phase composition. However, the application of these methods is limited by a small amount of synthesized material. The synthesis of magnesium ferrite particles using the mechanochemical method is a task that allows manufacturing powder material on a larger scale [14] but requires alternation of mechanical activation (MA) of the mixtures of iron and magnesium oxides and annealing at specific temperatures [15], under the control of MA parameters, atmosphere and the state of the product.

The physicochemical properties of composite materials are determined by the molecular and supramolecular structure of the polymer, by the concentration, structure, size and spatial arrangement of the particles filling it, by interphase states and interactions between particles. Precursors for composite protective materials are obtained by means of MA of a mixture of UHMWP and magnesium ferrite, which involves a significant increase in the surface of contact between the components, promoting the uniform distribution of inorganic particles in the polymer. This is an essential technological aspect for subsequent formation of the products, for example by means of hot pressing.

The goal of the work was to carry out mechanochemical synthesis and to study the structural and morphological characteristics of

MgFe_2O_4 and the composite material based on UHMWP, which incorporates the particles of the synthesized ferrite.

EXPERIMENTAL

Materials

The powders of magnesium oxide MgO (Ch. D. A. reagent grade – pure for analysis, sulphur-free, GOST 4526–75) and ferric oxide Fe_2O_3 (Ch. D. A. reagent grade, TU 6-09-5346–87) were used to synthesize MgFe_2O_4 .

To form the mechanocomposite of polymer/magnesium ferrite, we used UHMWP powder manufactured by Ticona GmbH (Germany), with particle size 100–160 μm and molecular mass $4 \cdot 10^6$ g/mol.

Synthesis procedure

Magnesium ferrite was synthesized in two stages: a stoichiometric mixture of magnesium oxide and ferric oxide was activated in an AGO-2 high-energy planetary ball mill (Russia) for 80 min. The vial volume was 250 cm^3 , ball diameter 5 mm, the mass of balls loaded into the vial was 200 g, the mass of sample under treatment was 10 g, the frequency of vial rotation around the common axis was ~1000 r.p.m. The activated oxide mixture pressed in tablets was annealed at a temperature of 1150 $^\circ\text{C}$ for 8 h in the air. The UHMWP/ MgFe_2O_4 composites were obtained by the joint MA of UHMWP and MgFe_2O_4 powders in AGO-2 for 2 min. The mass of the sample under treatment was 2 g, the total mass of balls was 100 g. The mass ratio (in per cent) of UHMWP/ MgFe_2O_4 in the mixture was 85 : 15.

To reveal the changes in the structure of UHMWP as a result of MA, its mechanical treatment in AGO-2 mill was carried out also for 2 min.

Methods of investigation

X-ray structural analysis was carried out with the help of an Empyrean diffractometer (PANalytical, the Netherlands) using a copper anode. The diffraction patterns of powder samples were recorded in Bragg-Brentano geometry with a step of 0.026° within angle range from 5 to 140° over 2θ , using a Ni filter at the diffracted beam and a two-coordinate detector Pixel3D. The phase analysis was carried out with the help of HighScore Plus software (PANalytical, the

Netherlands) using the crystallographic database ICSD PDF4. Calculation and refinement of the profile and structural parameters were carried out by means of the full profile analysis with the determination of coherent lengths (CL) and microstrain values according to the method proposed by Williamson–Hall [16].

Particle microstructure was studied by means of scanning electron microscope (SEM) with the help of a Quanta 3D FEG electron microscope (FEI Company, USA) in the high vacuum mode, which allowed us to obtain the images in secondary electrons using a high-resolution Everhart-Thornley detector (ETD). A specific feature of the investigation was in the analysis of topographic roughness, which may be carried out in detail only in the case of recording secondary electrons. The morphology of the samples over the recorded images was assessed using the IMAJEI software.

Thermal physical characteristics of the samples were studied by means of differential scanning calorimetry (DSC) with the help of a DSC8000 instrument (PerkinElmer, USA) in the inert atmosphere of Ar. DSC curves were recorded with a rate of 20 deg/min within temperature range 50–200 °C. For temperature measurements, the samples were pressed in aluminium standard cells to diminish the contribution from thermal resistance from the poor contact of the sample with capsule material. Temperature scale and thermal flux were calibrated on the basis of melt-

ing points (T_m) and the value of thermal effect (ΔH) of reference samples (PE samples) indium and zinc. The temperatures of the start, maximum (T_{max}) and completion of melting were determined from DSC curves.

RESULTS AND DISCUSSION

Magnesium ferrite $MgFe_2O_4$

Results of X-ray structural analysis of the stages of the synthesis of $MgFe_2O_4$ particles are shown in Fig. 1, *a*. After mechanochemical interaction of Fe_2O_3 and MgO for 80 min (see Fig. 1, *a*, curve 1), two strongly disordered structural modifications of $MgFe_2O_4$ are formed: cubic [98-024-0807] with grain size 7–8 nm and orthorhombic [98-009-408], which is usually formed at high pressure as a result of phase transitions, with even smaller grain size (this modification may be formed at the boundaries of the grains of cubic phase). Substantial widths of diffraction lines and their shift with respect to the positions for stoichiometric ferrite may be the evidence of either nonstoichiometric composition or nonuniform grain size distribution. In addition, not the whole amount of Fe_2O_3 interacts completely with MgO during MA: the reflections of hematite Fe_2O_3 with rhombohedral lattice [00-024-0072] (coherent length ~2 nm) remain in the diffraction pat-

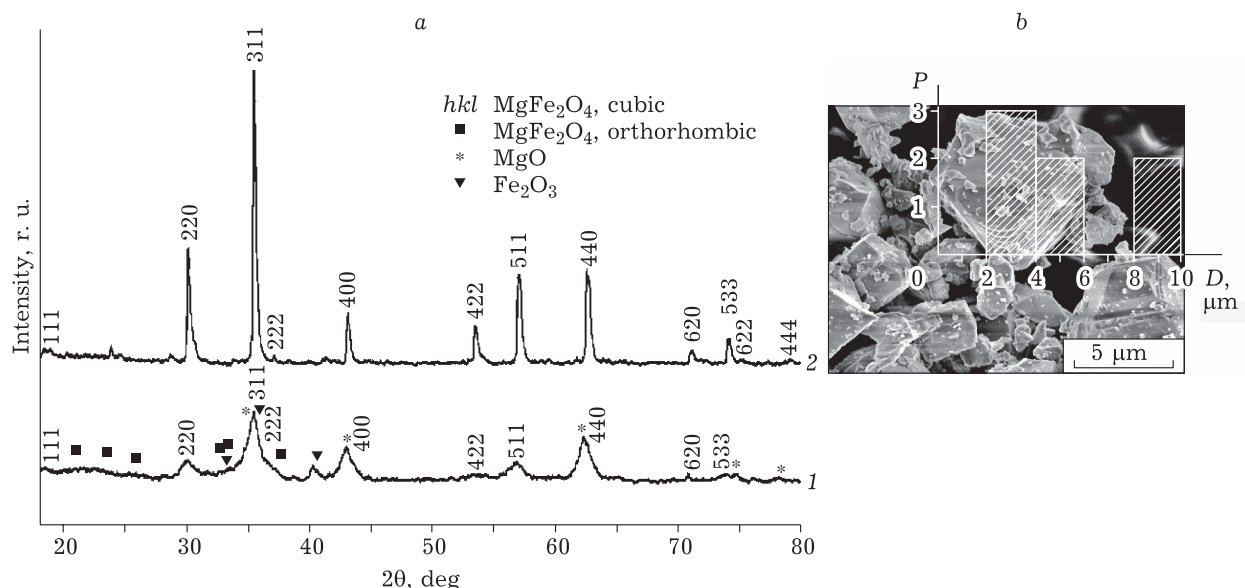


Fig. 1. Diffraction patterns (*a*) of the products of mechanochemical interaction of Fe_2O_3 and MgO before (1) and after annealing at 1150 °C (2); SEM image (distribution P over size D (μm) is shown in the insert) (*b*) of the particles of magnesium ferrite mechanically synthesized and annealed at 1150 °C.

tern. The traces of the initial MgO phase are present in the sample.

Annealing at a temperature of 1150 °C results in a more homogeneous phase composition (see Fig. 1, *a*, curve 2) and an increase in particle size. The major phase in the annealed sample is cubic MgFe_2O_4 . It is known that the lattice parameter a of stoichiometric MgFe_2O_4 is within the range 0.838–0.840 nm and depends on ordering degree, which is achieved in specific modes of thermal treatment. The lattice parameter of the mechanochemically synthesized MgFe_2O_4 sample was ~0.8367 nm, and the coherent length was >100 nm.

The SEM image of magnesium ferrite particles is presented in Fig. 1, *b*. The major part of well-faceted particles are 2–6 μm in size, though larger particles with a size of 8–10 μm are also present.

Ultra-high molecular weight polyethylene (UHMWP)

According to the data of X-ray structural analysis (Fig. 2, *a*), initial UHMWP is in the amorphous-crystalline state in which the crystal structure is represented by the orthorhombic phase with unit cell parameters $a = 0.74$ nm, $b = 0.493$ nm, $c = 0.254$ nm [17].

UHMWP crystallites are oriented mainly along the (110) plane as the intensity of the reflection corresponding to this plane is much higher than the intensities of the other reflections. The crystallite size is ~20 nm. After MA, the intensity of reflection (010), characteristic of the monoclinic structure, increases, which points to the change in the manner of molecule packing in the polymer and a decrease in coherent length to ~3 nm. This

may lead to the change of the internal structure of the polymer, and the interaction of the plastic polymer with solid MgFe_2O_4 particles may lead to additional molecular transformations [18].

According to SEM data, after MA for 2 min initially spherical UHMWP particles (see Fig. 2, *b*, image 1) change their shapes as a result of intense plastic deformation and become elongated, lamellar (see Fig. 2, *b*, image 2).

UHMWP/ MgFe_2O_4 mechanocomposite

X-ray phase analysis of the UHMWP/ MgFe_2O_4 composite (Fig. 3, *a*) revealed the absence of diffraction maxima of any new phases. Only broadened reflections of UHMWP and MgFe_2O_4 are present in the diffraction patterns, which is the evidence of a decrease in the size of grains of initial components.

According to SEM data (see Fig. 3, *b*) of the UHMWP/ MgFe_2O_4 composite, ferrite particles are surrounded by the polymer. The morphology of the polymer structure of a composite particle is layered, its size reaches 150 μm . The size of magnesium ferrite particles inside a composite particle remains almost unchanged.

DSC data for the MgFe_2O_4 sample under investigation shown in Fig. 4, *a* are characteristic of ferrites [19]: with an increase in temperature, thermal effect of recrystallization is observed, with the maximum at a temperature of ~340 °C, and a small thermal effect in the point of magnetic transition ($T_c = 470$ °C) [10].

According to DSC data (see Fig. 4, *b*), melting of the initial amorphous-crystalline structure of

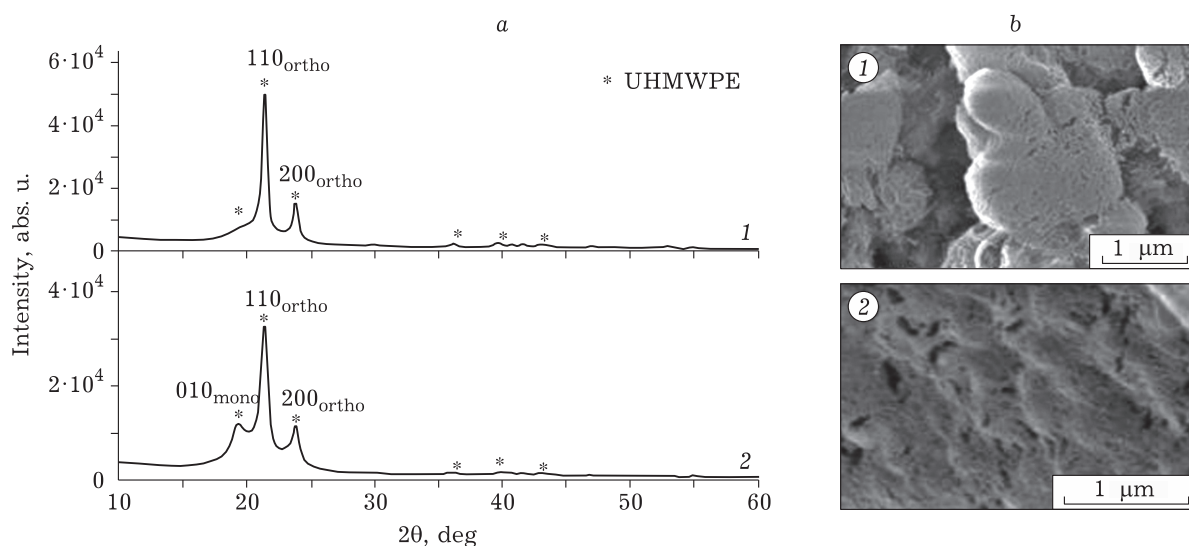


Fig. 2. Diffraction patterns (*a*) and SEM images (*b*) of UHMWP samples in the initial state (*1*) and after MA (*2*).

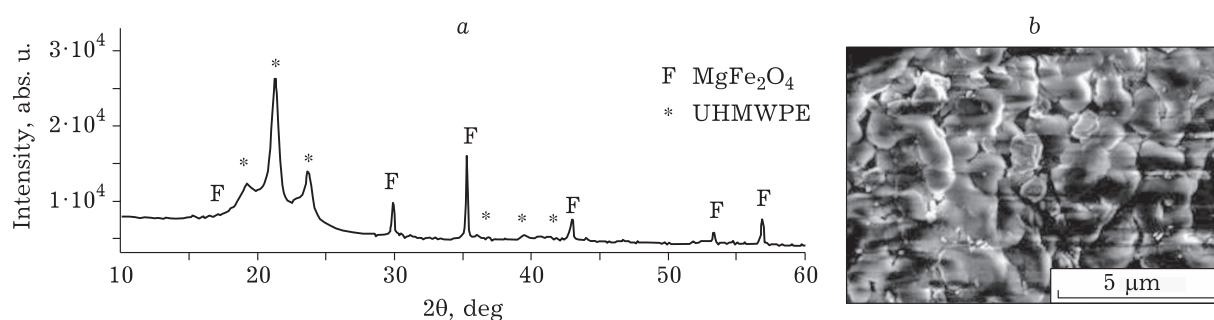


Fig. 3. Diffraction patterns (a) and SEM image (b) of mechanochemically synthesized UHMWP/MgFe₂O₄ composite.

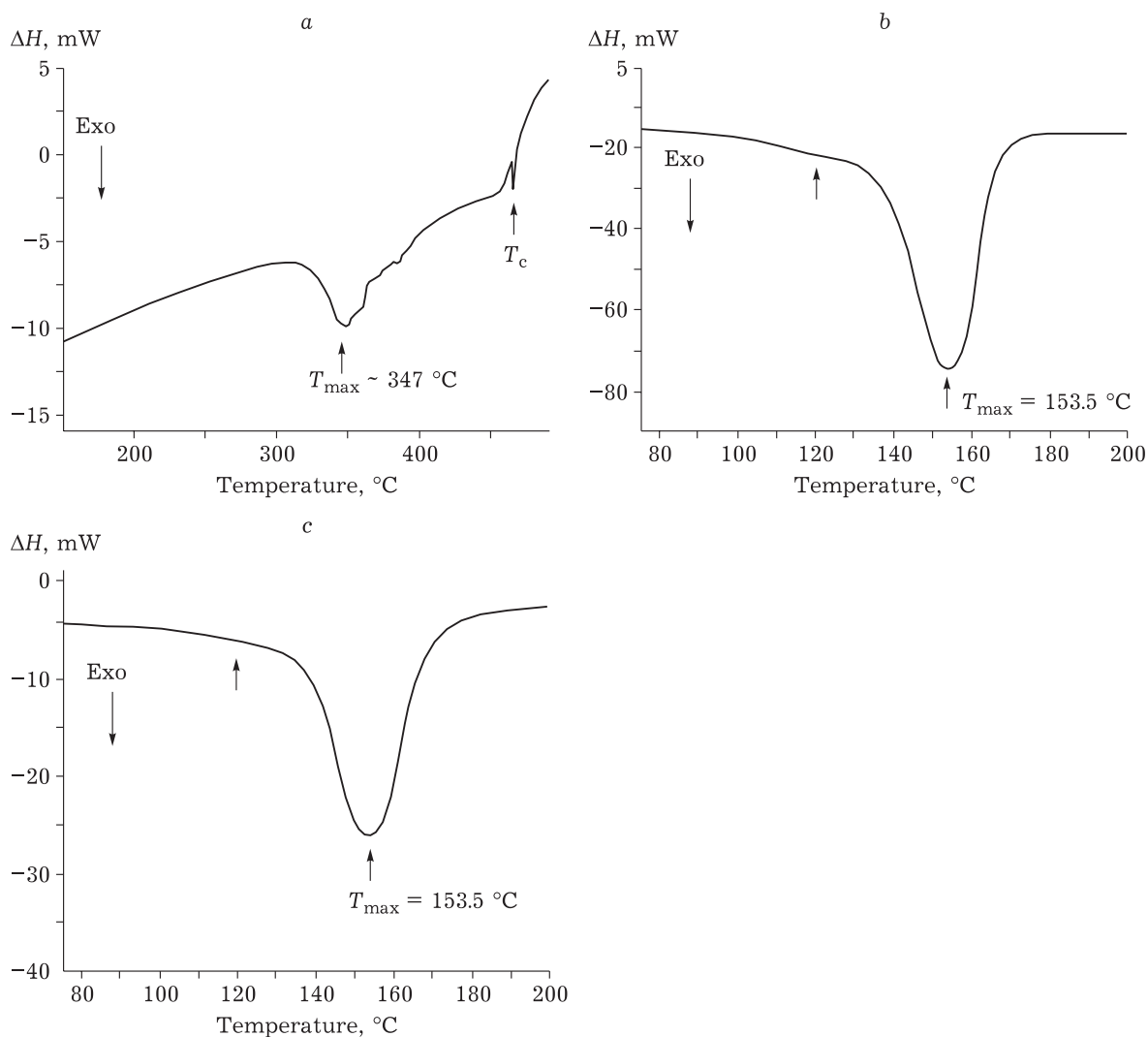


Fig. 4. DSC curves for initial MgFe₂O₄ (a), UHMWP (b) and mechanochemically synthesized UHMWP/MgFe₂O₄ composite (c).

UHMWP starts at 90–95 °C and is completed at ~180 °C. The major maximum is observed at 153 °C and a weak maximum appears at 120 °C. The latter maximum is the evidence of the existence of a polymer structure with a lower

melting point in the polymer. The thermal effect of melting is $\Delta H = 197.8$ J/g.

After the MA of UHMWP/MgFe₂O₄ the behaviour of melting exhibits no substantial changes. However, ΔH decreases and becomes equal to 122.4 J/g. The temperature region up to

the melting maximum has an extended tail without clear maxima (see Fig. 4, c).

It is known that the melting temperature of polymer materials depends on the size of lamellar crystals forming a supramolecular structure of the polymer. According to Thomson-Gibbs equation [20], lamellas of smaller size and lamellas with defects melt at a lower temperature than larger and defect-free ones do:

$$T_m = T_m^\infty (1 - 2\sigma_e / \Delta Hl)$$

Here T_m^∞ is the melting point of the lamellas of crystals of infinite size; σ_e is surface energy; ΔH is the heat of melting; l is the thickness of the lamellar crystal.

The existence of an extended tail on the DSC curve preceding the maximum of melting may be explained by the formation of a set of supramolecular structures with different melting points in the polymer as a result of the MA of plastic molecules with solid ferrite particles.

CONCLUSION

It is demonstrated that mechanochemical synthesis provides high dispersion and nanometer size of coherent lengths in MgFe_2O_4 . Mechanical activation of UHMWP leads to a change in its morphological characteristics. The joint mechanical activation of UHMWP with mechanochemically synthesized MgFe_2O_4 promotes an increase in the dispersion of ferrite particles and UHMWP, leading to the formation of the composite with a non-homogeneous distribution of ferrite particles inside the polymer and to the transformation of the supramolecular structure of the polymer.

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