Microelectronic Engineering 146 (2015) 85–91

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Layerwise laser-assisted sintering and some properties of iron oxide core/PEEK shell magnetic nanocomposites

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ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form 31 March 2015
Accepted 2 April 2015
Available online 25 April 2015

Keywords:
Selective laser sintering (SLS)
Superparamagnetic iron oxides
Polyetheretherketone (PEEK)
Tissue engineering scaffolds

ABSTRACT

Iron oxide nanoparticles ranging in average size from 42 to 235 nm were prepared by levitation jet aerosol synthesis. The nanoparticles were characterized by X-ray diffraction, BET measurements, and vibrating sample magnetometry. The selective laser sintering (SLS) process was proposed for fabrication and characterization of polymer nanocomposite based on nano oxides of Fe_xO_y type with biocompatible polyetheretherketone (PEEK) powder and manufacturing of porous tissue engineering scaffolds. The optimal regimes of laser sintering on the Nd^{+3}: YAG laser were carried out both with the applied external magnet field and without it. The influence of the external magnetic field led to ordering of the ferromagnetic nano oxides upon the polymeric matrix along the lines of the magnetic field, which could be useful for medical applications. Results on microstructural evaluation of ferromagnetic nano oxide samples were obtained using optical and scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray (EDX) analysis. The studies showed that both core–shell systems had the expected crystalline structure.

1. Introduction

Superparamagnetic iron oxide nanoparticles have a great potential for making tissue engineering scaffolds and drug delivery systems for the medical applications [1–5]. It can be used for magnetic particle hyperthermia process which is a highly specific and targetable method of localized remote heating of body tissues for the cancer treatment, and as an adjunct to radiotherapy and chemotherapy either [5,6]. Nevertheless the hyperthermia, as well as the vector drug delivery, the separation of physiological-active substances, introductions of magnetic diagnostic markers require new approaches, which ensure a reproducible obtaining of a number of the most important magnetic nanoparticle characteristics. They include: predetermined chemical and phase composition; stable structural, physical and/or toxicological nanoparticles features; size of nanoparticles specifying the value of the saturation magnetization, coercive force and the ability of a nanoparticle to penetrate into the tissue; surface modification type, which determines the ability of joining with the protein molecules or shaping of additional shielding shell with the assigned functional characteristics; anisotropy of particle's shape, which changes the effectiveness of magnetocaloric heating and the hydrodynamic conditions for the transfer into the bloodstream and other physiological liquids. The range of materials being currently tested as candidates for magnetic hyperthermia is rather wide, still ferrimagnetic iron oxides, maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), have become the common choice, for the following reasons [5]: their better chemical stability against oxidation than that of metal nanoparticles; high magnetization; less induced oxidative stress toxicity in vivo; relatively well known metabolism and Food and Drug Administration approvement for use in humans.

There are two most commonly used methods for preparing highly dispersed iron oxide nanoparticles, they are thermal decomposition of iron organometallic compounds and co-precipitation of aqueous iron salts (chlorides, nitrates, etc) in basic media. Besides, also known is a reproducible and potentially scalable microwave-based method to make stable citric acid coated multi-core iron oxide nanoparticles, with exceptional magnetic heating parameters [7]. The acute problem is an aggregation prevention, which significantly levels the potential advantages of the materials use in the ultra-dispersed state. One of the methods for this problem solution is the isolation of nanoparticles into the inert matrices, where they do not undergo aggregation, "aging" and can be controllably released with the retention of chemical and phase composition. It was aimed to design and develop fully biodegradable and magnetic nanocomposite substrates for bone tissue engineering

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http://dx.doi.org/10.1016/j.mee.2015.04.030
0167-9317/

consisting of a poly(ε-caprolactone) PCL matrix reinforced with bioresorbable iron-doped hydroxyapatite (FeHA) nanoparticles [8]. The idea to develop magnetic scaffolds for additional control of angiogenesis in vivo was considered by Bock et al. [9], where magnetic scaffolds were manufactured through a dip coating of scaffolds in aqueous ferrofluids that contained iron oxide nanoparticles coated with different polymers for biomedical applications.

As a method for conservation of magnetic particles, the selective laser sintering (SLS) is a promising technique for fabricating of the functional medical devices and graded structures with nano additives [10]. But a direct SLS fabrication of the scaffolds from the nano powders by multilayered techniques is a difficult technological task. Sintering is well known to be a thermally activated process, accompanied by coagulation of the nanoparticles into the micro-sized conglomerates. Nevertheless, 3D nanocomposite PCL/FeHA scaffolds with interesting magnetic properties and specific architecture were developed in [11] but on the bioplotter dispensing machine. Stabilization of the nanoparticles in a polymeric matrix and additionally reinforced porous structure [12,13] makes it possible to arrange a desired distribution of the nanoparticles in the polymer and thus to protect them from oxidation and corrosion and even to design functionally graded (FG) structures. Moreover, the polymer can be used to coat the iron particles and increase their circulation time in the bloodstream by evading the reticuloendothelial system [1]. The results suggest that nanoparticles mechanically reinforced the polymer matrix; the elastic modulus and the maximum stress increased by about 10% and 30%, respectively [14]. But the maximum strain decreased by ~50%; this testified to an enhanced brittleness.

Finally, the correlations "the prehistory of obtaining (i.e. "background") – the chemical composition of the particle's volume and surface condition – phase/structural composition – morphology – magnetic properties" will determine the nanoparticle's behavior after the polymer dissolution in the physiological liquids, including the external magnetic and/or electric fields. Earlier [13] we demonstrated how a laser-assisted technique of the 3D synthesis was used to prepare a porous core shell polycarbonate structures containing encapsulated nickel and/or copper nanoparticles distributed heterogeneously over the sintered polymer and dangerous for cancer tissue. The current development of magnetic hyperthermia is heavily focused on two aspects, namely the composition of nanoparticles (where reproducibility and scalability are consistently found to be hard to achieve), and the instrumentation needed for applying external fields to generate the magnetic hyperthermia and for measuring of the resultant heat deposition in tissues.

At the present study before preparing by levitation jet aerosol synthesis the nanoparticle properties were examined. The SLS process was used for fabrication and characterization of the reinforced polymer nanocomposite based on nano oxides of Fe_xO_y type with biocompatible polyetheretherketone (PEEK) powder and manufacturing of iron oxide core/porous shell magnetic targeting systems.

2. Experimental procedures

Using a Gen levitation jet generator described in details elsewhere [15,16], we obtained Fe/Fe_xO_y aerosol nanoparticles. To this end, a 0.3 mm diameter iron wire situated in a quartz tube of 14 mm inner diameter was introduced into an RF inductor encasing the tube. The end of the wire was heated by electromagnetic field of a countercurrent inductor to formation of a levitating liquid droplet and onset of metal vaporization. The droplet was blown by helium or argon at a constant gas flow rate and fed with the source wire at regular time intervals, as the metal vaporized.

The polyetheretherketone (PEEK – Victrex Co., UK) was bought at the chemical market, and used as supplied. The size of the particles taken for the polymer fractions was 60–70 μm that was comparable with the laser beam diameter. It ensured a high stacking density of the particles in the initial metal-polymer composition (MPC) that resulted in its qualitative sintering. The PEEK was dried before mixing. The Fe/Fe_xO_y aerosol nanoparticles were used as a filling material. Polymer mixtures with nano iron particles were prepared in the 100:1, 50:1 and 10:1 ratios by wt. (the first of the ratios is for the PEEK). The MPC was placed into a hermetically sealed container filled with metallic balls of different diameters ranging from 0.2 to 0.5 mm and shaken by a Czechoslovak "Chirana" vibrator during 6 h for achieving uniform compositions.

A cw Nd^{+3}: YAG laser was used to carry out the SLS process. The beam power P ranged between 4 and 10 W. The laser beam scanned the powder mixture surface; separation between laser beam passages (70 μm) was close to the diameter of the laser beam. The optical facility had a focal length of 147 mm and a 25-mm shift from the bottleneck. Layer-by-layer laser sintering process was performed in a specially designed camera under Ar or in air as described elsewhere [10].

The structure of the sintered porous PEEK matrices with incorporated nanoparticles of iron oxides was studied by optical microscopy (NEOTHOT 30 M, Carl Zeiss) and SEM/EDX (LEO 1450 microscope, Carl Zeiss, equipped with an EDX analysis, INCA ENERGY 300, Oxford Instruments).

The crystal structure of the nanoparticles was examined by X-ray diffraction on a DRON-3M powder diffractometer (Fe K_α radiation). Their phase composition was determined using JCPDS PDF data (PCPDFWIN ver. 2.02, release 1999) and the Crystallographica SearchMatch ver. 3.102 program. Rietveld analysis (PowderCell 2.0 Program) of X-ray diffraction patterns was used to evaluate the ratio of crystalline phases in the nanoparticles.

The specific surface area of the nanoparticles was obtained by four point nitrogen physical sorption BET measurements using a META SORBI-M instrument. Magnetic characteristics of the powders were measured in magnetic fields of up to 0.8 MA/m under room temperature using an M4500 vibrating sample magnetometer (EG&G PARC, USA).

3. Results and discussion

Table 1 shows the main specific parameters of the synthesized nano particles series F02-F07: density – ρ (column 3); X-ray diffraction (XRD) composition (column 4); a specific saturation magnetization – σ_s (column 5); a specific remanent magnetization – σ_r (column 6); a coercivity – H_c (column 7) and specific surface area – S (column 8) depending on the average particle sizes d (column 2).

Specific surface areas varied in a range from 4.65 (F02) to 27.3 (F07) m^2/g; density from 4.97 (F04) to 5.48 (F02) g/cm^3; the saturation magnetization from 33.7 (F03) to 91.9 (F05) emu/g and could be different by XRD data. The high magnetization was for the F07 nanoparticles – 27.8 emu/g and the magnetization lower – 4.63 for the F02, whereas high coercivity was – 292 Oe for the F03 and low one – for the F04 and F06 (175 Oe). Our values are comparable with the results obtained in [2], when ferromagnetic iron oxides had similar but low specific magnetic moments of about 20–30 emu/g. For improvement of such situation Qiang et al. [2] proposed a new approach to synthesize monodispersed core–shell nanostructured clusters with high specific magnetic moments above 200 emu/g. The opened problem is that pure metallic iron nanoparticles are highly sensitive to oxidation and dissolution through electrochemical reactions. By the data of specific surface areas S (m^2/g) of the samples of the various