Processing of Magnetic Beads for Biological Sensor Application by Pyrolysis of Metal Containing Polymers

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A method based on pyrolysis of polymers containing atoms of basic ferromagnetic elements Fe, Co and Ni was applied for the formation of beads containing magnetic nanocrystallites. Structure, microstructure and magnetic properties of the materials were characterized. It was found that the application of frontal polymerization and further pyrolysis enables the formation of composite beads consisting of Co, Fe_3C or Ni spherical nanocrystallites stabilized in carbon matrix. The matrix is built of amorphous carbon and graphite. The bead's size can easily be further reduced, by about 50-90%, using ball milling. The magnetic properties of the beads depend on the crystallite type and the volume fraction of the metallic component. Extracts on the basis of composites containing Fe_3C showed no cytotoxicity, whereas those containing Co and Ni exhibited negligible cytotoxicity for the test article/vehicle ratios 6.25 and 3.125 mg/ml. The beads may potentially be used as biological sensors.

Keywords: Magnetic beads; magnetic nanocomposites; ferromagnetic nanoparticles.

El método basado en pirólisis de polímeros con contenido de elementos ferromagnéticos básicos como Fe, Co y Ni fue utilizado para la formación de bolas con nanocristalitos magnéticos. La estructura, microestructura y propiedades magnéticas de los materiales son característicos. Se ha encontrado que la aplicación de la polimerización frontal permite la creación de bolas compuestas con nanocristalitos esféricos de Co, Fe_3C o Ni estabilizados con matriz de carbono. La matriz está formada por carbono y grafito amorfo. El tamaòo de las bolas podrá ser luego reducido fácilmente en un 50-90% mediante la moltura de las mismas. Las propiedades magnéticas de las bolas dependen del tipo del cristalito y de la fracción de volumen del componente metálico. Los extractos a base de compuestos con contenido de Fe_3C no tienen citotoxicidad, mientras que los que contienen Co y Ni demostraron una citotoxicidad insignificante en las pruebas de artículos/vehículo del orden de 6.25 y 3.125 mg/ml. Las bolas pueden ser potencialmente usadas como sensores biológicos.

Descriptores: De bolas con nanocristalitos magnéticos; magnéticos nanocompuestos; ferromagnéticos nanocristalitos.

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1. Introduction

Studies on the application of nanoparticles in medicine were recently developed due to the number of suitable features they represent, such as high specific area and the ability of interacting with a broad variety of tissue. The most rapidly developing group is the family of magnetic nanomaterials, which provides a broad application area, both *in vivo* and *in vitro*. Among the most important applications one can mention detection and analysis of bioparticles, targeted drug delivery, contrast material for magnetic resonance imaging and hyperthermia. The scope of the research comprises fabrication methods of nanoparticles, their stabilization, methods of their functionalization, biocompatibility tests and problems of vesicular transport. The important issue is a proper choice of the size of the magnetic carriers, which determines their access to blood vessels, which have sizes in a broad range from 30 μm up to 2.5 mm [1]. From this point of view the nanoparticles should be as small as possible, however, in such a case the forces acting on the particle in an external magnetic field, which are proportional to its volume, may be too small.

In biomedical applications the nanoparticles can exist as individual crystallites [2] or be incorporated in biocompatible beads [3-8].

Several methods can be used for fabrication of magnetic nanoparticles. Among the most frequently used ones, one can mention electric arc dispersion [9], synthesis from microemulsions, polymerization of colloidal solutions containing metal and monomer ions, zol-gel methods and pyrolysis of metal containing polymers [3-8].

The magnetic properties of nanoparticles are determined by their sizes. Below a certain size, usually 5-15 nm, the single domain particles, undergo a transition into the superparamagnetic state, which is characterized by lack of magnetic hysteresis and saturation magnetization characteristic of a ferromagnetic material. These properties are very convenient because the particles do not attract each other without a presence of an external magnetic field. However, the particles may agglomerate anyway tending to reduce the surface energy, loosing that way the superparamagnetic properties.

In this study the method based on pyrolysis of polymers containing atoms of basic ferromagnetic elements Fe, Co and Ni was applied for formation of beads containing magnetic nanocrystallites. Structure, microstructure and magnetic properties of the materials were characterized. The beads may potentially be used as biological sensors.

2. Experimental

The acrylamide metal complexes (MeAAm) (Me=Co, Ni, Fe) were obtained by substitution reaction of inorganic hydrates by the acrylamide. Frontal polymerization was carried out at atmospheric pressure in self-generated atmosphere. The nanocomposites were formed by further pyrolysis. More detailed description of the processing route, as well as the products, can be found in [10].

The structure of the material, after all stages of preparation, was studied by X-ray diffraction (XRD) (Rigaku Miniflex, Cu-K$_\alpha$), Mössbauer and Raman spectroscopy. Microstructure was analyzed using scanning electron microscope (SEM) (Hitachi 3500) and High Resolution Electron Microscope (TEM) JEOL JEM 3010. The hysteresis loops were recorded in a temperature range 90-300 K, in an external magnetic field of $\pm$ 1600 kA/m.

3. Results and discussion

The processing of the nanocomposites comprised the formation of an appropriate metal containing monomer (complex) - MeAAm, followed by its frontal polymerization and further pyrolysis of the polymer [10]. The pyrolysis temperatures were chosen on a basis of differential scanning calorimetry (DSC) tests and were, depending on the material type, in the range of 773-1073 K. The pyrolysis products were in a form of powder particles (beads), having broad distribution of sizes in a range of few to hundreds of micrometers. Ball milling of the powders, for 60 min. in a shaker mill, resulted in a noticeable size reduction accompanied by the narrowing of the size range. Table I presents the change of the bead's size resulting from the ball milling. One can see that the most noticeable reduction of the bead's size (about 90%) was achieved for the CoAAm and NiAAm material. Moreover, the milling generally, especially for the CoAAm and NiAAm, reduces the agglomeration.

The products of frontal polymerization were amorphous. Pyrolysis of metal containing polymers leads to the formation of nanocrystallites. The XRD tests, performed on the pyrolysed polymers containing initially atoms of Co, Fe and Ni, showed formation of nanocrystallites of βCo, Fe_3C and Ni, respectively (Fig. 1). The pyrolysis temperatures were: 773 K for Co, 873 K for Ni and 1073 for Fe.

Application of Raman spectroscopy revealed that the matrix of all the beads consists of amorphous carbon and graphite. On the patterns shown in Fig. 2 one can observe two, characteristics of carbon, bands G and D (1590 and 1347 cm^{-1}, respectively). Their shape and intensity proves a presence of the both types of carbon. The bands at the wave numbers 215, 280, $\sim$400 and $\sim$600 cm^{-1} are characteristic of hematite, Fe_2O_3, which apparently forms on the surface of the nanocrystallites [11,12].

TABLE I. Mean size of the beads [μm] in the as-pyrolysed state and after ball milling.

Precursor type	As-pyrolysed	After ball milling
CoAAm	48	4
FeAAm	50	23
NiAAm	112	19

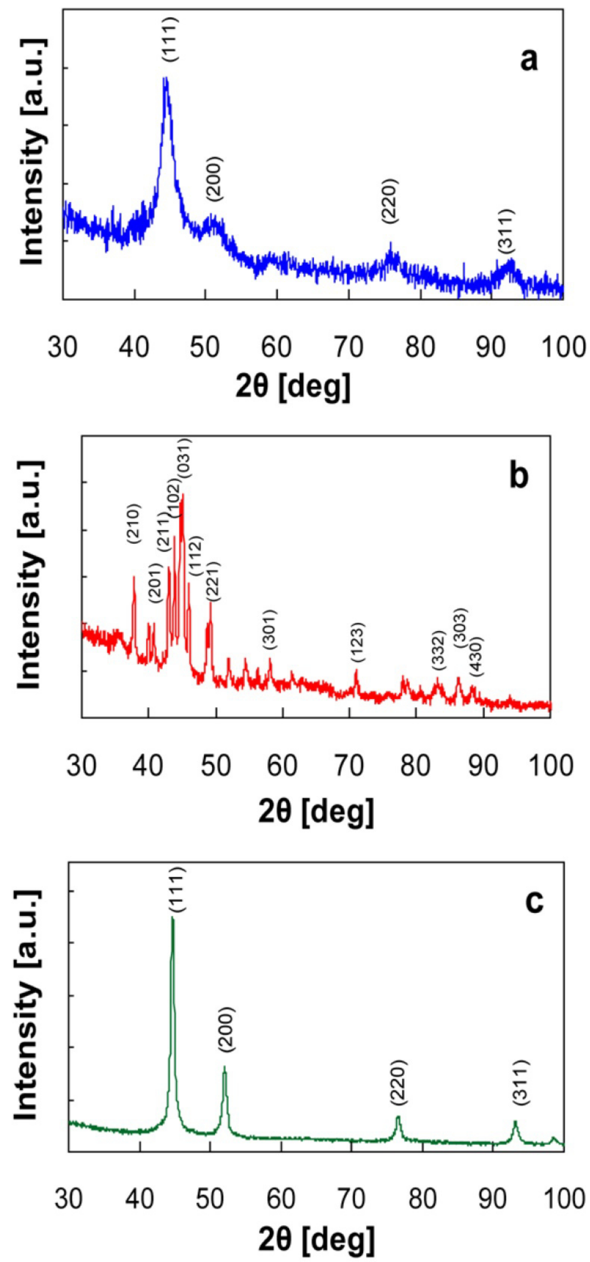

FIGURE 1. XRD patterns of pyrolysed specimens on a basis of Co – a, Fe – b and Ni – c precursors.

The carbon matrix encapsulates the nanocrystallites, protecting them from oxidation and agglomeration. The magnetic nanocrystallites are dispersed within the volume of the carbon beads.

The crystallites of Co, Fe_3C and Ni had spherical shape and sizes 10, 20-80 and 15 nm, respectively (Fig. 3). The content of the magnetic component in the beads, which was

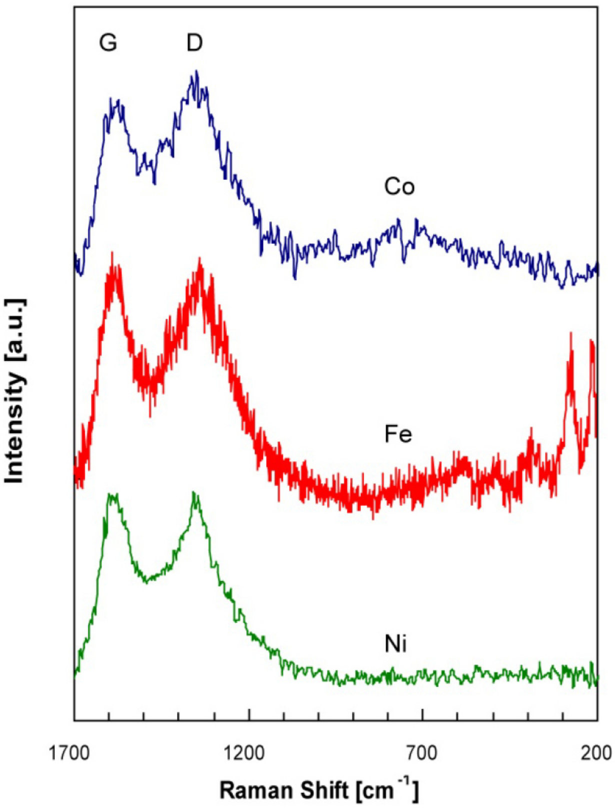

FIGURE 2. Raman spectra of pyrolysed specimens on a basis of Co, Fe and Ni precursors.

calculated from the magnetization values, was for Co, Fe_3C and Ni nanocrystallites 12, 22 and 24 wt.%, respectively.

The room temperature magnetic properties of the beads are summarized in Table II and the hysteresis loops are presented in Fig. 4. The coercivity depends on the material microstructure and composition. For the elementary metals, Co and Ni the coercivity is in the range of kiloampers per meter, which suggests that some carbon must have been dissolved in the metals. For the intermetallic phase Fe_3C the coercivity is obviously much higher due to the more complex structure. The saturation magnetization depends on both, the material type and fraction of the magnetic component. The latter depends on the pyrolysis temperature. The remanence is controlled jointly by the coercivity and saturation magnetization.

Studies of the magnetic properties after ball milling showed a reduction from 10% for the elementary metals to 2% for the Fe_3C.

TABLE II. Room temperature magnetic properties of the nanocomposite beads containing nanocrystallites of Co, Fe_3C and Ni.

Crystallite type	Pyrolysis temp. [K]	Coercivity [kA/m]	Remanence [emu/g]	Saturation magnetization [emu/g]
Co	773	6.7	3.6	19.8
Fe_3C	1073	40.2	8.2	38.7
Ni	873	3.6	1.3	13.2

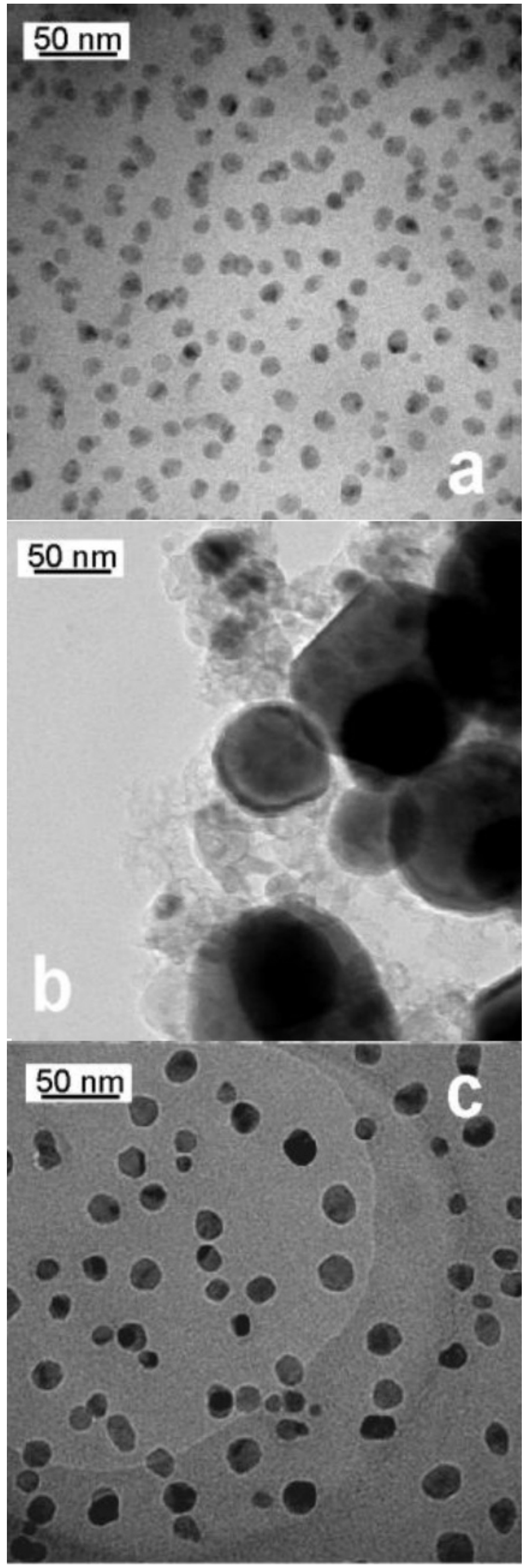

FIGURE 3. TEM microstructures of the nanocomposite beads showing nanocrystallites of Co – a, Fe_3C – b and Ni – c.

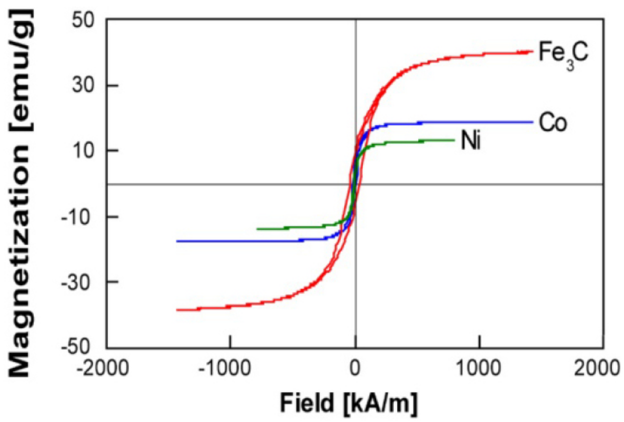

FIGURE 4. Room temperature hysteresis loops for the beads containing nanocrystallites of Co, Fe_3C and Ni.

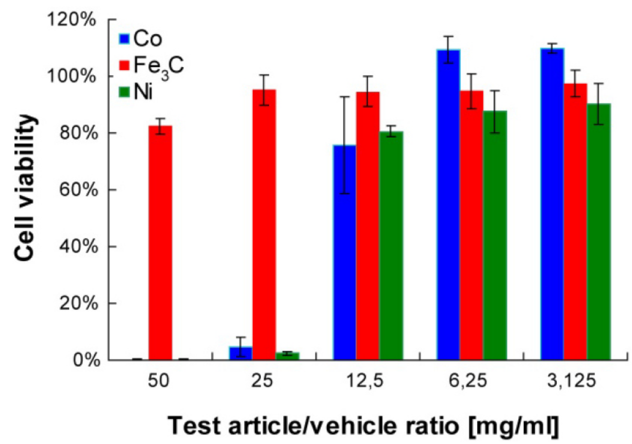

FIGURE 5. Cells viability extraction concentrations 50, 25, 12.5, 6.25 and 3.125 mg/ml for the beads containing Co, Fe_3C and Ni nanocrystallites.

In Fig. 5 the results of the XTT test for the materials containing Co, Fe_3C, Ni nanocrystallites are shown. The extraction vehicle consisted of DMEM supplemented with L-glutamine and antibiotic. Under the condition of the tests, extracts on the basis of the composites containing Fe_3C showed very low cytotoxicity with a maximum percentage of the cell reduction of 18 % for the highest test article/vehicle ratio, *i.e.* 50 mg/ml. The XTT test results, for the beads containing Co and Ni crystallites, showed that their extracts caused a much higher cell mortality. However, the extracts of the lowest test article/vehicle ratios, *i.e.* 6.25 and 3.125 mg/ml, were apparently much less toxic.

4. Conclusions

The following conclusions can be drawn from the studies:

Application of frontal polymerization and further pyrolysis enables formation of composite beads consisting of Co, Fe_3C or Ni spherical nanocrystallites stabilized in carbon matrix. The matrix is built of amorphous carbon and graphite. The bead's size can easily further be reduced, by up to 90%, using ball milling. The ball milling causes deterioration of the magnetic parameters by a few percent.

The magnetic properties of the beads depend on the crystallite type and the volume fraction of the metallic component.

Extracts on the basis of composites containing Fe_3C showed no cytotoxicity, whereas those containing Co and Ni exhibited negligible cytotoxicity for test article/vehicle ratios 6.25 and 3.125 mg/ml.

Acknowgledgement

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1. T. Sandor and D.F. Adams, *Am. J. Roentg.* **132** (1997) 433.
2. C. Brigger, C. Dubernet, and P. Couvreur, *Adv. Drug. Deliv. Rev.* **54** (2002) 632.
3. M. Ławecka *et al.*, *J. Nanoparticle Research* **5** (2003) 373.
4. M. Ławecka *et al.*, *J. Alloys and Compounds* **369** (2004) 244.
5. E. Sówka, M. Leonowicz, B. Andrzejewski, A.D. Pomogailo, and G.I. Dzhardimalieva, *J. Alloys and Compounds* **423** (2006) 123.
6. E. Sówka *et al.*, *Physica B* **384** (2006) 282.
7. E. Sówka, M. Leonowicz, B. Andrzejewski, A.D. Pomogailo, and G.I. Dzhardimalieva, *J. Alloys and Compounds* **423** (2006) 123.
8. E. Sówka *et al.*, *J. Magn. Magn. Mater.* **316** (2007) 749.
9. M. Leonowicz *et al.*, *Materials Letters* **60** (2006) 442.
10. A.D. Pomogailo and G.I. Dzhardimalieva, *Polymer Sci. Ser. A.* **46** (2004) 250.
11. G. Magnacca *et al.*, *Chem. Mater.* **15** (2003) 675.
12. H. Namduri and S. Nasrazatani *Corrosion Science* **50** (2008) 249.