UNIVERSITY OF MEDICINE AND PHARMACY OF CRAIOVA

DOCTORAL SCHOOL

PhD THESIS

(Abstract)

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Magnetisable nanoparticles: production and assembly for technical and biomedical applications

(ABSTRACT)

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CONTENTS

I. PRODUCTION OF NANO-MICROSYSTEMS THROUGH PHYSICAL PROCESSES

By physical processes, the nanoparticles have been obtained through the vaporisation method (in vacuum or in gas), the production of nanoparticles in plasma and by the laser method.

• The vacuum vaporisation method is characterised by the ability to collect a large amount of metal particles;

• The particles obtained are polydisperse. Their average size is inversely proportional to the amount of energy supplied per sample length unit;

• Achievement of the pressure of about 10^{-7} torr on the premises is difficult (under continuous operation). The pressure on the premises does not depend only on the performance of the pumps and traps used, but also on the rate of gas desorption by the solid surfaces on the premises, especially by the evaporator and evaporating substance.

• Production of metal particles through the method of vaporisation into gas starts from a certain value of the gas pressure on the vaporisation chamber, namely:

- for molybdenum, $500 \cdot 10^{-3}$ torr;
- for copper, $400 \cdot 10^{-3}$ torr;
- for copper, $700 \cdot 10^{-3}$ torr;

• Through variations of the pressure on the vaporisation chamber, at values higher than the corresponding minimum pressure in the previous string, changes in the shape and size of the molybdenum, copper and cobalt particles take place.

• The plasma with temperatures of up to $3 \cdot 10^{4}$ K is obtained in continuous current plasma generators;

• the plasma temperature, speed and gas-kinetic pressure can be controlled by adjusting the intensity of the discharge electrical current;

• The use of helium and hydrogen in combination with argon leads to metal evaporation speeds of up to one million times higher than the case of pure argon plasma;

• The diameter of the nanoparticles produced in the plasma can be controlled by adjusting the plasma gas pressure in the evaporation chamber. Through the MIG process, we obtain particles of sizes comparable to those obtained through the method of metal evaporation into gas (10... 60 nm), in helium environment at pressures of 0 MPa.

• The laser vaporisation of metal samples is done for values $E < E_S^V$;

• The value of the energy E_S^V is inversely proportional to the absorbance A of the metal target;

• The ceramic nanoparticles of β-SiC and γ-Al_2O_3 can be produced from ceramic plates of α-SiC and Al_2O_3 in argon atmosphere (0.1 MPa);

• In nitrogen atmosphere (0.1 MPa), TiN, ZnN, VN, Ta_2N, Nb_4N_3 and Mn_4N nanoparticles are produced. Al and AlN nanoparticles are also produced. Nitrogen compounds with Fe, Ni, Cu, W, Mo and Si are thermodynamically unstable at room temperature.

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II. PRODUCTION OF IRON PARTICLES THROUGH PLASMA PROCESSES

The production of iron nanoparticles through plasma procedures can be done in several ways. We used:

1. production of nanoparticles by electric arc and plasma processes;
2. production of cavitation nanoparticles by plasma jet processes and/or transferred plasma arc;
3. production of iron microspheres through plasma jet processes;

The particles thus obtained have an

1. octopus shape.

Their average sizes are:

- for the nucleus: diameter: 12 μm; wall thickness: 0.5 μm;
- for tentacles: length: 188 μm; equivalent diameter: 2 mm; wall thickness: 0.35 μm.

2. Microtubules characterised by: length: 100 μm, diameter: 27.64 mm and respectively wall thickness: 0.25 mm.

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III. EQUIPMENT FOR THE PRODUCTION OF MAGNETISABLE NANO-MICROPARTICLES AND IN THE FORM OF METALLURGICAL SLAG SPHERES

In this chapter, we present our invention to our research and invention teams, which refers to a specialised equipment intended for the production of magnetisable nano-microparticles, in the form of spheres, destined to the production of intelligent materials [1-6] and environmental protection, by processing the metallurgic slag under a plasma jet.

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IV. MAGNETORHEOLOGICAL SUSPENSIONS: PRODUCTION AND PROPERTIES

Fluids made of magnetisable nano-microparticles dispersed in fluid matrices are referred to as magnetisable nano-microsystems in fluid phase. They are known in the literature as magnetorheological suspensions [1 – 3] (MRS). The liquid matrix is the fluid medium where the magnetic phase is dispersed. It consists of a base liquid and miscible surfactants:

Magnetorheological suspensions based on silicone oil, stearic acid and iron microparticles obtained by us were analysed:

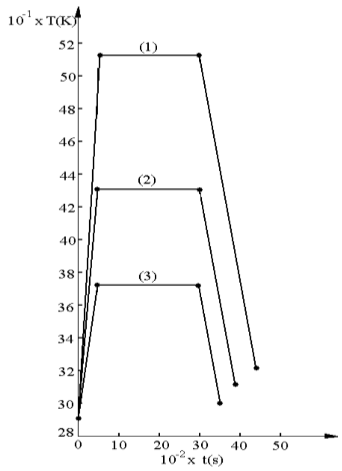

Figure 84. Temperature-time chart

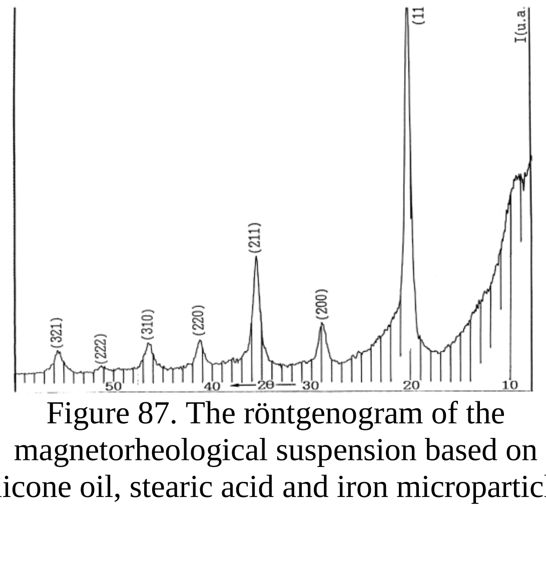

Figure 87. The röntgenogram of the magnetorheological suspension based on silicone oil, stearic acid and iron microparticles

The rheological properties of the suspensions were determined with the MRD 180 (Physica 9 type) re-viscometer.

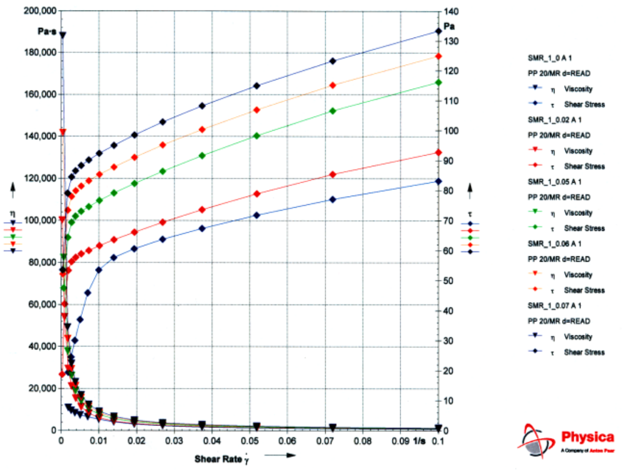

Figure 103. The rheological properties of the suspensions were determined with the MRD 180 (Physica 9 type) reviscometer

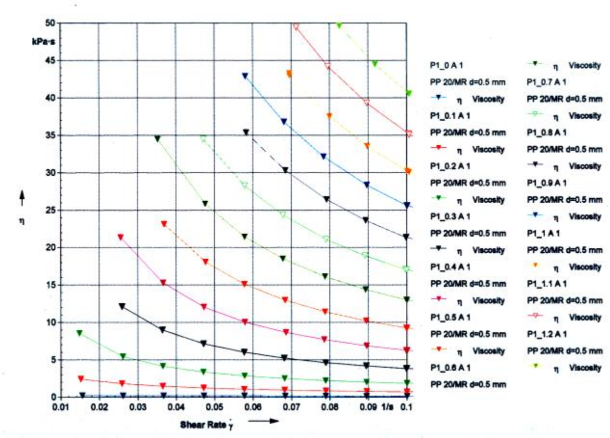

Figure 104. The rheological properties of the suspensions were determined with the MRD 80 (Physica 9 type) re-viscometer

We also obtained magnetorheological suspensions based on silicone oil, guar-gum and iron $Fe_2(CO)_9$ microparticles.

- The dimensional distribution of microparticles may be adjusted by choosing the optimal temperature for the thermal decomposition of $Fe_2(CO)_9$;
- The thermal decomposition of $Fe_2(CO)_9$ in silicone oil with stearic acid and in inert medium causes the surface of particles to be free of oxides;
- The magnetic properties of the suspension depend on the volume concentration of the solid phase. The suspension obtained is a soft magnetic material;
- The rheological properties of the suspensions obtained depend on the volume concentration of the solid phase, on the intensity of the magnetic field applied and respectively the deformation speed.

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V. MAGNETICALLY RESPONSIVE MATERIALS IN THE SOLID PHASE

The magnetorheological (MR) materials are a class of intelligent materials the mechanical, electrical and magnetic properties of which change drastically when applying a magnetic field. Magnetorheological suspensions (MRSs), magnetorheological elastomers (MREs) and magnetorheological gels (MGs) are part of family of MRs.

A magnetodielectric material based on MRS-hybrid was made, which consists of a polyurethane foam sponge, magnetorheological suspension and magnetorheological elastomer.

It has been shown that the relative dielectric permittivity and the factor of dielectric losses of MRS-hybrid change with the frequency of the electric field applied. It has also been shown that by applying a magnetic field at a fixed frequency of the electric field, the dispersion and dissipation of the electricity increases sensitively and in a programmed manner.

Using the dipolar approximation, we developed a theoretic model explaining the effects of the magnetic field applied on the dispersion and dissipation of the electric field of low and mediul frequency for a perfectly elastic MRS hybrid. The theoretic model is qualitative. It describes the physical processes driving the MR effects in the MRS hybrid.

These effects make it possible to apply the MRS-hybrid in the devices where the dispersion and dissipation of electricity are required to be preset.

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THE INFLUENCE OF THE MAGNETIC FIELD ON THE MAGNETOELASTIC STATE AND RELATIVE DIELECTRIC PERMITIVITY OF THE HYBRID MAGNETORHEOLOGICAL ELASTOMER

The magnetorhetological elastomer (MREh) achieved in the paper is a hybrid. It consists of a magnetorheological elastomer based on silicone rubber and iron carbonyl and an electrorheological elastomer based on elastomer polyurethane and TiO_2 particles. At the interface between the two components, by diffusion of components, a composite elastomer has been achieved. In magnetic field, MREh changes its relative dielectric permittivity. It increases with the intensity of the magnetic field and is sensitively influenced by the amount of TiO_2 used. In return, the elasticity constant remains constant as the magnetic field increases, but decreases as the amount of TiO_2 increases. By applying the magnetic field, MREh is generally compressed. Thus, for without TiO_2 the compression is limited up to intensities of the magnetic field of 400 kA/m. A value from which the hybrid expansion occurs by increasing the magnetic field intensity. By adding TiO_2, MREh is compressed linearly with increasing the magnetic field, but the compression value is determined by that of the TiO_2 amount for the same value of the applied magnetic field intensity.

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PARAFFINE, CARBONYL IRON AND GRAPHENE BASED COMPOUNDS MAGNETODIELECTRIC EFFECTS

The solid solution consisting of (P) in a mixture of (nGr) and (CI) powder is a magnetodielectric. In magnetic field, the capacity of condensers have different growth directions when increasing the H intensity of the magnetic field, as the volume concentration of (CI) is higher or lower than (P). If in the case of the S_1 sample the relative dielectric permittivity decreases when increasing the intensity of the magnetic field, in the case of the S_2 sample, the relative dielectric permittivity increases with the intensity of the magnetic field applied. In both samples, the electric conductivity increases along with increasing the intensity of the magnetic field. In the S_2 sample, due to the concentration of (CI), lower compared to the S_1 sample, the installation of the elctric conductivity is done from increased value of the intensity of the magnetic field.

The theoretical model drafted perfectly explains the experimental data only for S_2.

In return, for S_1, as a result of the magnetisable phase agromerisation, a decrease of the relative dielectric permittivity occurs along with the intensity of the magnetic field applied.

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VI. POROUS MEMBRANES

The membranes were born from the need for fine and ultrafine filtering of fluid substances. By copying nature, membranes were made based on metal [1, 2] ceramic materials [3], polymers [4], liquid materials [5], etc. The S_1, S_2 și S_3 membranes are studied with Nanoscope 53, equipped with SPIP 1.11 [10]. On the images obtained (figure 137), pores penetrating the membranes could be observed.

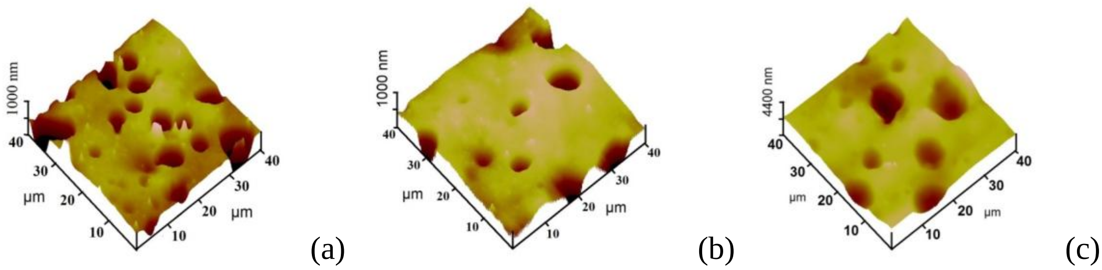

Figure 137. Porous membranes: (a) S_1, (b) S_2, (c) S_3

- The membranes based on silicone rubber, silicone oil, stearic acid and catalyst, obtained by the process shown in item 2.1. are 420 μm thick and have pores.
- The dimensional distribution of pores is caused by the supersaturation with air (gas) of the liquid solution.
- By increasing the catalyst concentration, the SR gelling time is decreased and implicitly of the liquid solution with consequences on the air bubble kinematics. Thus, for the same value of the air supersaturation of the liquid solution, the size of the pores is influenced by the amount of catalyst used.
- The mechanisms described can be useful in preparing the technology for manufacturing the pore membranes based on SR, SA and C.

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THE INFLUENCE OF THE CATALYST ON THE DISPERSION CHARACTERISTICS AND ABSORPTION ON THE ELASTOMERIC MEMBRANES WITH PORES IN THE ELECTRIC FIELD OF MEDIUM FREQUENCY

The membranes formed of SR, SAS and C have pores. The characteristics of absorption, dispersion, distribution of pores and average diameter thereof depend on the volume concentration of the catalyst. We consider that membranes can be useful when separating the phases, using electrical methods.

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VII. MATERIALS PROTECTING AGAINST RADIATIONS

The materials with properties of absorbing the corpuscular and electromagnetic radiations, **characterised by that which** when immersing in elastic matrices of industrial, medical synthetic rubber type, and/or absorbent sponges a solid phase in the form of nano-microparticles of carbonyl iron, iron, gadolinium, lead, aluminium, graphene, carbon, organometallic compounds or combinations thereof, sheets of various areas and thicknesses for the achievement of equipment for protection against corpuscular and electromagnetic radiations or hybrid materials of hybrid type according to figure 150, achieved from a porous membrane wherein the nano-microparticles of iron, gadolinium, lead, aluminium, graphene, carbon, organometallic compiunts or combinations thereof are absorbed, which are in a liquid matrix (mineral oils, water based soluble compounds, light water or heavy water), over which magnetorheological elastomers are polymerised with specific additives with adjustable transmission of corpuscular and/or electromagnetic radiation and which have the response function controlled in magnetic, electrical field, mechanical forces or combinations thereof.

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VIII. CONTRIBUTIONS AND PERSPECTIVES

The topic of "**Magnetisable nano-microparticles**": **production and assembly for technical and biomedical applications"**, chosen for the PhD thesis is generous by its very formulation. Using fine and ultrafine powders when manufacturing various solutions for healing different wounds and/or in treating diseases is known since ancient times. In this paper, the preparation of fine powders is brought to scientific level, referred to in the literature as nano-particles and fine powders, called microparticles.

By adding additives specific to the absorption of radiations, elastic material was made, which was used to manufacture protective clothing for high energy therapies and diagnosis with X rays. They are the subject of the patent application registered at OSIM under the no. A/0071 of 01. 11. 2016. The thesis in this form does not exhaust the topic approached. Following this confidence, we suggest below a few perspective guidelines on the intelligent materials with biomedical applications,

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