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VERSATILE PECVD PROCESS FOR PREPARATION OF IRON-BASED MAGNETIC NANOPARTICLES

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Introduction

Iron-based nanoparticles attract much attention of the materials science community due to their unique magnetic, physical and chemical properties and great application potential [1]. The properties of nanoparticles sized under 100 nm differ significantly from bulk materials, e.g. the melting point, surface tension and chemical reactivity depend on surface/bulk atom ratio. Also a superparamagnetism occurs when the size of the nanoparticles drops below critical size leading to the formation of single magnetic domain. One practical use of the magnetic nanoparticles is in ferrofluids – magnetic liquids with parameters like flow, viscosity, shape etc. controllable by external magnetic field. Other breakthrough is expected in magnetic recording media allowing much higher recording density. Nanopowders with inherently large surface area also open new trends in catalysis. Another important branch of applications are biomedical applications using nanoparticles as targeted drug delivery agent [2], MRI contrast agent [3], tumor hyperthermia etc.

There are several ways to produce nanoparticles besides wet chemical processes. Nanoparticles can be produced by various processes, e.g. thermal decomposition, laser pyrolysis [4], plasmachemical processes [5, 6], etc. In this work, we focus our attention on plasma enhanced chemical vapour deposition (PECVD) synthesis, since this single–step method offers an advantage in its simplicity, low environmental impact, lack of solvents and surfactants, etc.

In order to produce nanopowders in desirable amount, size distribution and chemical composition, it is essential to carefully control the process of plasma synthesis. By changing the composition of the working atmosphere, we were able to prepare nanoparticles with chemical composition ranging from pure iron Fe over various iron oxides and suboxides up to fully oxidised iron(III) oxide Fe_2O_3 in sufficient amount.

Experimental

For synthesis of nanoparticles, we used microwave plasmachemical reactor operating at low pressure. Experimental set-up is shown in Fig. 1. The discharge was maintained in fused silica tube 1 m long and 5 cm in diameter at reduced pressure in argon – oxygen mixture. The operating frequency of the microwave generator was 2.45 GHz and maximum output power was 1.5 kW. Microwave energy in waveguide was transferred into the plasma using an applicator – surfaguide Sairem SURFG 439. We used iron pentacarbonyl $Fe(CO)_5$ as a precursor for the iron-based nanoparticles. The precursor vapours were introduced into the discharge, where the dissociation took place, breaking away carbonyl groups. The iron atoms consecutively agglomerated, forming a nanopowder – nanoparticulate crystalline matter. The powder was collected on filters placed between the plasma reactor and a rotary pump. The composition of nanopowder product strongly depended on the composition of the working atmosphere, especially the amount of oxygen in the working gas. Currently we are producing 5 g of nanopowder during 10 minute experiment run but further upscaling should be relatively straightforward.

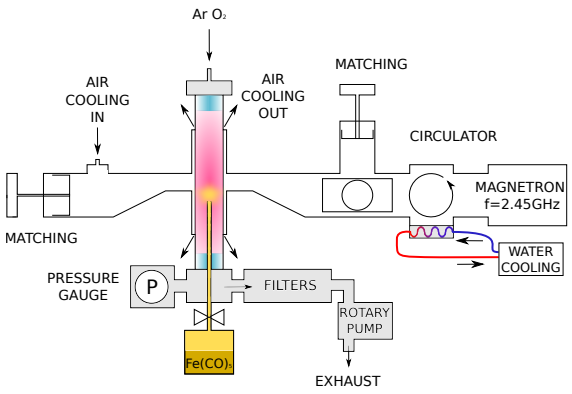

Fig. 1: Experimental arrangement.

Results and discussion

The process of synthesis of iron-based nanoparticles is dependent on several experimental parameters like microwave power, composition and pressure of the operating atmosphere, velocity of gas flow etc. We decided to investigate the influence of working gases on chemical and morphological composition of the resultant product.

The nanopowder sample LP#16 prepared in pure argon plasma consisted of pure iron $\alpha-$Fe and iron(II,III) oxide Fe_3O_4, weight ratio determined by X-ray diffraction (XRD), as seen in Fig. 2, is 81:19. The average size of the crystals was 14 nm for iron and 4 nm for iron oxide. The simplest explanation is that iron nanoparticle is covered by iron oxide forming core–shell nanocomposite. This claim is supported by a transmission electron microscopy (TEM) image shown in Fig. 3. The thin layer of iron oxide on iron nanoparticle is formed due to high reactivity of pure iron nanoparticles which tend to oxidise easily. However, the formation of oxide effectively passivates the nanoparticle and so the oxidation appears only in the surface layer.

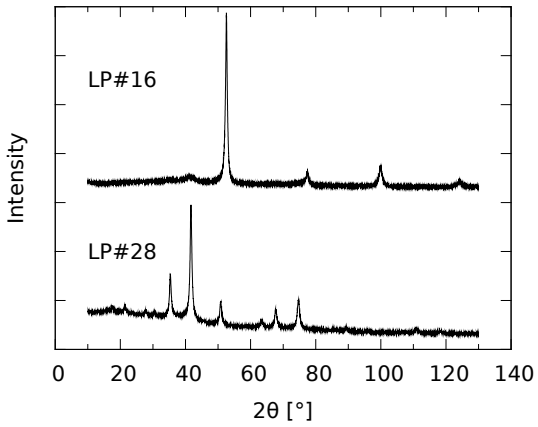

Fig. 2: XRD analysis of both samples.

Another sample LP#28 was synthesised in argon–oxygen mixture plasma creating pure iron(III) oxide Fe_2O_3 (wt. 100%). The average size of the crystallites was estimated to be 14 nm. Iron from the precursor oxidised in the reaction vessel immediately due to the presence of sufficient amount of oxygen in the working atmosphere. This is different process than in sample LP#16 where initially pure iron nanoparticles are secondarily oxidised.

Conclusions

In this article, we present the PECVD synthesis in microwave discharge as a simple way to produce iron-based nanoparticles in single-step technological process. The nanopowder was prepared in argon and argon–oxygen plasma at reduced pressure.

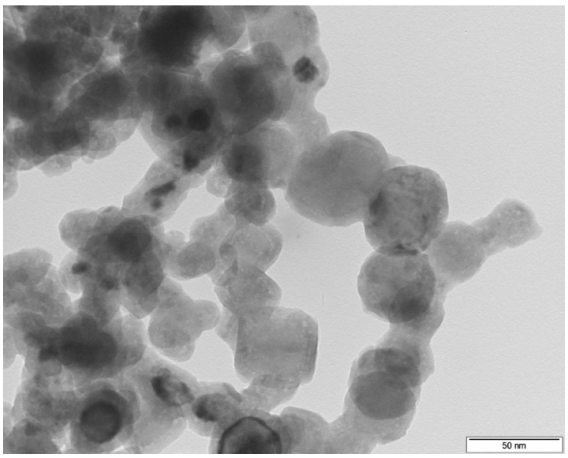

Fig. 3: A TEM image of sample LP#16.

Depending on the working atmosphere, the chemical composition of the powder varied from pure iron Fe to fully oxidised iron oxide Fe_2O_3. The iron originating from the precursor dissociation had only a little chance to oxidise in argon plasma containing oxygen only from the carbonyl group CO. However, the iron atoms in oxygen rich plasma were fully oxidised to iron(III) oxide. Certainly, there should be a set of conditions, when the product is mostly iron(II,III) oxide Fe_3O_4.

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