Synthesis of iron based magnetic nanoparticles

O. Schneeweiss[1], B. David[1], T. Zak[1], R. Zboril[2], and M. Mashlan[2]

[1]*Institute of Physics of Materials AS CR, Zizkova 22, 61662 Brno, Czech Republic*
[2]*Faculty of Science, Palacky University, Svobody 26, 770 46 Olomouc, Czech Republic*

Iron based nanoparticles are very interesting materials for magnetic circuits, catalysis, and other industrial and medical applications. Nanoparticles of iron oxides, particularly γ–Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite), have captured a dominant position especially due to their superior chemical and thermal stability, hardness, non-toxicity and biocompatibility. These properties are combined with the excellent magnetic behaviour and large surface area [1]. Metallic iron based nanoparticles are characterized by high saturation magnetization and high Curie temperature combined with superior catalytic properties in various reaction systems. They have a drawback in their chemical stability due to a rapid oxidation process. Fe-Co and namely Fe-Ni alloys have better resistance against oxidation than pure iron and they form a basis of several excellent soft magnetic materials. The classical alloying or powder metallurgical processing yield polycrystalline materials with mean grain sizes above one micrometer.

The nanocrystalline materials can be prepared by several physical and chemical methods. The physical methods are usually based on fast vapour condensation and subsequent fast cooling which stops a grain growths. As examples the classical procedure by Gleiter [2], an evaporation and cryo-condensation process [3], or spark synthesis [4] can be mentioned. Common disadvantage of the physical methods is their high cost low rate production.

There are also several chemical methods which can be used for preparation of nanocrystalline materials. Precise methods are based on sol-gel procedure, e.g. [5], but they are limited by expensive precursors and technology. Very promising are the thermal induced solid state synthesis, e.g. [6,7]. Preparation of nanoparticles by thermally induced solid state reactions requests precursors of amorphous or nanocrystalline structure. The main reason is that the structure and phase transformations of amorphous and nanocrystalline materials occur at lower temperatures (in comparison with coarse polycrystals) where a crystal growth is still very slow.

The processing based on using ferrihydrite as precursor are presented as the example of preparation and properties of the iron oxides and iron based metallic nanocrystals by thermally induced solid state reactions. In the first step of the processing, temperatures and kinetics of phase transformations in vacuum and different atmospheres were investigated by measurements of temperature dependence of magnetic moment. The phase composition, structural and magnetic properties, particle size and morphology of the samples prepared in optimized reaction conditions in vacuum (10^{-1} Pa), pure hydrogen, and ethylene were studied by X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectroscopy. Under optimized time and temperature, hematite nanoparticles were prepared by heating in vacuum, while magnetite and α-Fe were obtained by annealing in hydrogen at 265 and 350°C, respectively. Heat treatment in ethylene resulted in the formation of Hägg carbide particles. When an additional precursor containing Ni or Co, e.g., Ni or Co oxalate, is mixed with the ferrihydrite in an appropriate ration, nanocrystalline Fe-Ni or Fe-Co alloy can be obtained using similar slightly modified technology.

The magnetic properties of the annealing products were tested by measurements of hysteresis loops. For example, spherical magnetite nanoparticles (mean coherent length ~30 nm) revealed in the Mössbauer spectrum a well-defined structure with the ratio of tetrahedral to octahedral Fe sites being 1/2 and high saturation magnetization (~ 95 Am^2kg^{-1}) which is close to a bulk material. However, the Verwey transition of the magnetite nanocrystals was found about 80 K. For the α-Fe nanoparticles (mean coherent length ~60 nm) saturation magnetization 201 Am^2kg^{-1} and coercive force 22.6 kAm^{-1} were obtained. The shape of the hysteresis loop corresponds to interacting isolated particles.

The relatively simple technology based on application of the ferrihydrite as the precursor can yield various magnetically ordered iron based nanocrystalline materials. An addition of other precursors of alloying elements allows to prepare alloys with mean coherent length bellow 50 nm.

Key words: nanocrystalline powder, iron, iron oxides, nickel, cobalt

References.

[1] R.M. Cornell, U. Schwertmann: The iron oxides. Structure, properties, reactions, occurrence and use, VCH, Weinheim, 1996, p.1.

[2] H. Gleiter, Nanocrystalline materials, Progress in Mater. Sci. 33 (1989) 223-315.

[3] C. Duhamel, Y. Champion, M. Tenceb, M. Walls, Synthesis of controlled-chemistry ultrafine Fe_xNi_{1-x} ferromagnetic powders, J. Alloys Comp. 393 (2005) 204-210.

[4] O. Schneeweiss, Y. Jiraskova, J. Sebek, Preparation and properties of Mg–Fe nanocomposite phys. stat. sol. (a) 189 (2002) 725-729.

[5] G. Ennas, A. Falqui, G.Paschina, G. Marongiu, Iron-Cobalt Alloy Nanoparticles Embedded in an Alumina Xerogel Matrix, Chem. Mater. 17 (2005) 6486-6491.

[6] R. Zboril, M. Mashlan, D. Petridis, Iron(III) oxides from thermal processes-synthesis, structural and magnetic properties, Mossbauer spectroscopy characterization, and applications, Chem. Mater. 14 (2002) 969-982.

[7] M. Hermanek, R. Zboril, M. Mashlan, L. Machala, O. Schneeweiss, Thermal behaviour of iron(II) oxalate dihydrate in the atmosphere of its conversion gases, J. Mater. Chem. 16 (2006) 1273.

Corresponding author: O. Schneeweiss, Institute of Physics of Materials AS CR, Zizkova 22, 61662 Brno, Czech Republic, e-mail: schneew@ipm.cz, fax: +420 541218657.