

USE OF COLD PLASMA FOR TRANSFORMATION OF IRON NANOPARTICLES

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1. Introduction

Plasma is called the fourth state of the matter. Plasma contains a certain portion of free electrons and the atoms are partly ionized. The presence of negative and positive carriers of the charge makes plasma¹ electrically conductive and distinguishes it from gaseous state.

The plasma that contains a very small part of the ionized particles (approximately 1 %) is named cold (nonthermal) plasma. The cold plasma is generated in a high-voltage electric field, and although the velocity of electrons is strongly dependent to the temperature up to a few thousands degrees of Celsius, their effect on the plasma temperature is low and final plasma temperature is close to the temperature of the surrounding.

Cold plasma plays an important role in a variety of technologies, i.e. particularly plasma activation serves to alter or improve adhesion properties of surfaces prior to coating, painting, etc. Cold plasma systems have become also a very important tool for nanotechnology processing including semiconductors, thin films and the production of polymers and the modification of the materials.

In this paper, the cold plasma has been used to initialize an oxidation process of iron nanoparticles.

2. Materials and methods

Iron nanoparticles, used as a precursor, were prepared by a spark discharge^{2,3}. The carbon shell protects these iron nanoparticles from spontaneous oxidation. The oxidation process has been performed in a laboratory cold plasma-chemical reactor. The iron nanoparticles were placed on an electrode for 20 seconds of the exposition time and the reactor was activated with maximal power. The iron nanoparticle precursor and final iron oxide product were characterized by TEM⁴, BET⁵, XRD and Mössbauer spectroscopy⁶.

2.1. Transmission Electron Microscopy (TEM)

Transmission Electron Microscope JEOL 2010 F – type high contrast (HC) was used to determine the size and morphological properties of the initial iron nanoparticles and final

nanoparticles. Accelerating voltage of 200 kV and magnifications from 100000 to 400000 times were used in these measurements.

The preparation of the sample is the key moment in the TEM application. The nanopowder was added into the ethanol and exposed to ultrasonic waves. Then, one drop of the suspension was placed on a 300 mesh copper grip, which was coated with holey carbon film. Finally, the sample was dehydrated at room temperature.

The local electron diffraction was used for a determination of the phase composition of the nanoparticles.

2.2. BET method

A specific surface area of the dispersive or porous materials can be determined by the BET method. The BET (Brunauer-Emmett-Teller) method is based on the measuring the adsorbed gas quantity. The adsorption-desorption isotherm was obtained by nitrogen adsorption using a Sorptomatic 1990 (ThermoFinnigan) surface area analyzer. The specific surface area of this sample was determined by the multipoint BET3 method in the p/p_0 range between 0 and 0.5. Sample was de-gassed at room temperature with a pressure of 10^{-6} for 24 h.

2.3. Mössbauer Spectroscopy

Mössbauer spectroscopy was applied to determinate the iron phase composition of initial and final materials. ⁵⁷Fe Mössbauer spectra were measured by a standard transmission method in a constant acceleration mode with a ⁵⁷Co (Rh) radioactive source. The spectra were collected at room temperature. The values of the isomer shift are related to α -Fe at room temperature. For computer processing of the spectra, a NORMOS package was used yielding the values of the relative spectrum area RA and the values of the hyperfine parameters including the hyperfine magnetic field B, isomer shift δ_{Fe} , quadrupole splitting Δ and quadrupole shift ϵ .

2.4. X-ray powder diffraction (XRD)

XRD was also used for a determination of the phase composition of the samples. An X'Pert PRO instrument with a Co K α radiation was employed for the XRD analyses. The phase composition of the samples was evaluated using an X'Pert HighScorePlus software package (PANalytical®) and the JCPDS PDF-4 database.

3. Results and Discussion

At first, the initial iron nanoparticles were characterized. TEM gave information about the size and morphology of the iron nanoparticles as well as the thickness of the carbon preservation shell has been estimated.

We can see that the iron nanoparticles form agglomerates (see Fig. 1). A more detailed Fig. 2 shows that they have a ball-shaped profile and their sizes vary from 15 to 100 nm. Individual particles are covered with a carbon preservation envelope. Its thickness is estimated to 8 nm. The fact that the core and the shell of the nanoparticles are composed of iron

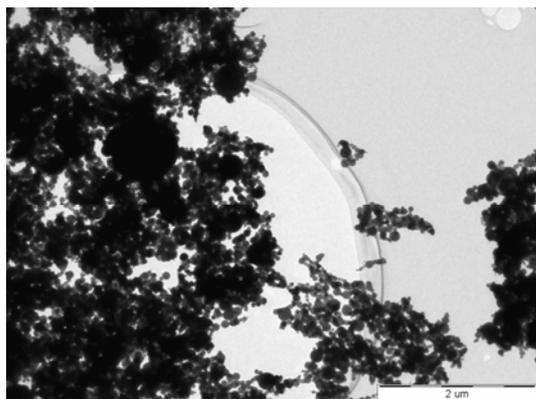


Fig. 1. TEM picture of the initial iron nanoparticles

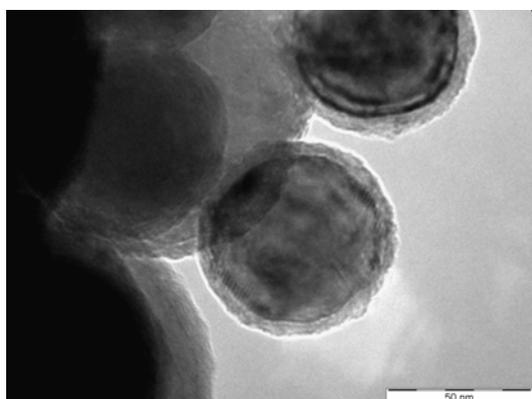


Fig. 2. Detailed TEM picture of the iron nanoparticles covered by a carbon preservation shell

and carbon, respectively, has been confirmed by local electron diffraction.

From the adsorption-desorption isotherm (dependence of the V_{ads} on p/p_0) (Fig. 3), it was determined, that this material is nonporous with the surface area of $7.3 \text{ m}^2 \text{ g}^{-1}$.

RT Mössbauer spectrum (see Fig. 4) contains one sextet with $\delta_{\text{Fe}} = 0 \text{ mm s}^{-1}$, $\varepsilon = 0 \text{ mm s}^{-1}$ and $B = 33 \text{ T}$, well corresponding to alpha iron.

XRD (Fig. 5) pattern confirms that the initial material does not include any other iron-bearing phase.

The changes of the phase composition as well as changes of the morphology particles were observed after oxidation initialized by a cold plasma.

RT Mössbauer spectrum of the final product (see Fig. 6) consists of $\alpha\text{-Fe}$ sextet ($\delta_{\text{Fe}} = 0 \text{ mm s}^{-1}$, $\varepsilon = 0 \text{ mm s}^{-1}$, $B = 33.0 \text{ T}$, $\text{RA} = 24 \%$), $\alpha\text{-Fe}_2\text{O}_3$ sextet ($\delta_{\text{Fe}} = 0.37 \text{ mm s}^{-1}$, $\varepsilon = -0.16 \text{ mm s}^{-1}$, $B = 51.6 \text{ T}$, $\text{RA} = 46 \%$), two sextets of Fe_3O_4 ($\delta_{\text{Fe}} = 0.27 \text{ mm s}^{-1}$, $\varepsilon = 0 \text{ mm s}^{-1}$, $B = 49.2 \text{ T}$, $\text{RA} = 14 \%$ and $\delta_{\text{Fe}} = 0.66 \text{ mm s}^{-1}$, $\varepsilon = 0 \text{ mm s}^{-1}$, $B = 45.7 \text{ T}$, $\text{RA} = 12 \%$) and FeO doublet ($\delta_{\text{Fe}} = 0.93 \text{ mm s}^{-1}$, $\Delta = 0.73 \text{ mm s}^{-1}$, $\text{RA} = 4 \%$).

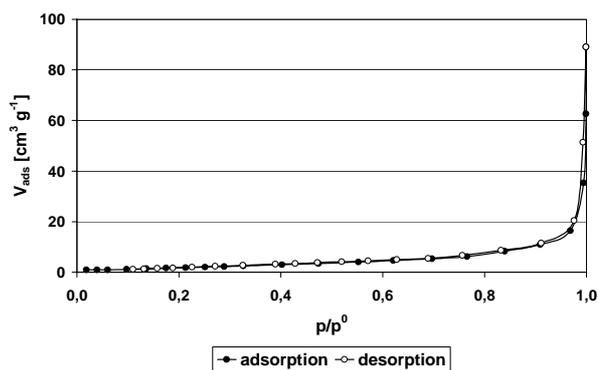


Fig. 3. Adsorption-desorption isotherm of the iron nanoparticles covered by a carbon preservation shell

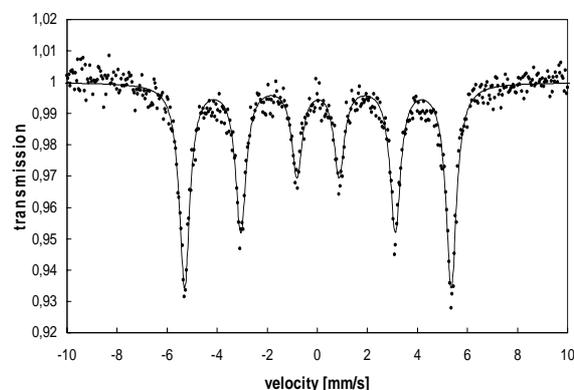


Fig. 4. The RT Mössbauer spectra of the iron nanoparticles

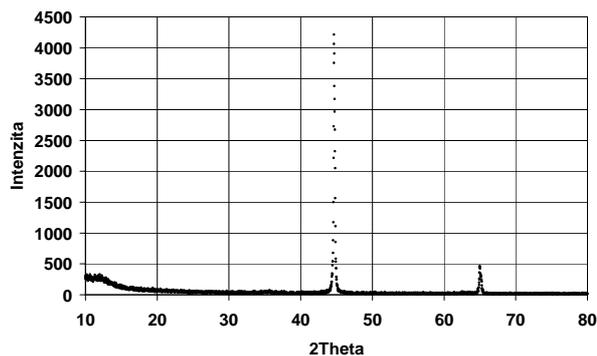


Fig. 5. XRD pattern of iron nanoparticles

The presence of all the iron phases identified by Mössbauer spectroscopy was confirmed also by XRD (see Fig. 7).

TEM shows that the sizes of the nanoparticles of final

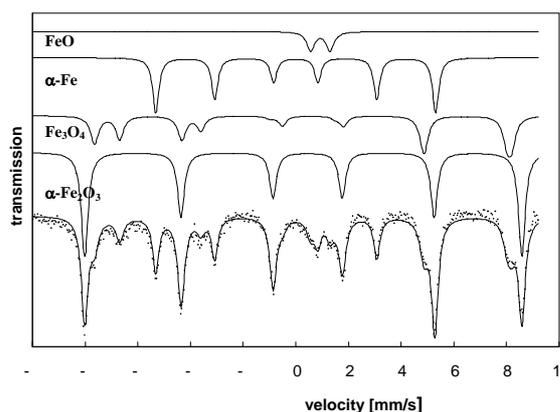


Fig. 6. RT Mössbauer spectrum of the final product

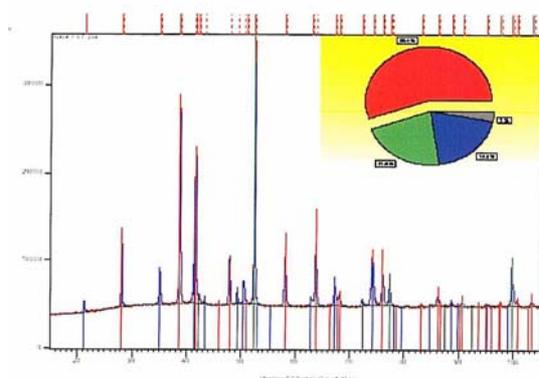


Fig. 7. XRD and pattern list of the final product

product are the same as the sizes of the nanoparticles of the initial system, but some nanoparticles have changed the ball-shaped form (see Fig. 8). At the same time, we can see that the carbon preservation cover is disturbed and nanoparticles form certain clusters (see Fig. 9). The local electron diffraction shows on one hand that the core of the carbon preserved nanoparticles contains iron. On other hand, the core of the nanoparticles with the disturbed carbon shell contains iron oxide.

4. Conclusion

The initialization of oxidation process of iron nanoparticles by the cold plasma was studied. It is obvious that the cold plasma disturbs the carbon preservation shell of the nanoparticles and these nanoparticles are continuously oxidizing. α - Fe_2O_3 (hematite), Fe_3O_4 (magnetite) and FeO (wüstite) were identified in the final product. On one hand, the nanoparticles with disturbed carbon cover oxidize, but on other hand, they

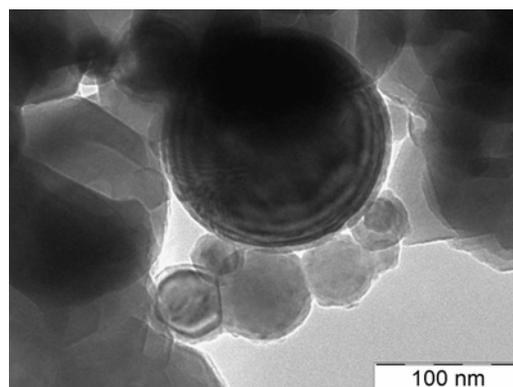


Fig. 8. TEM pictures of the nanoparticles of the final product

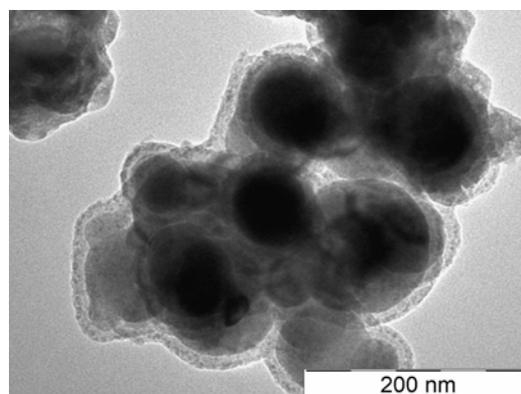


Fig. 9. Clustering of the nanoparticles with the disturbed carbon cover

arrange into irregular clusters in which iron and iron oxide were observed. It thus seems that there exists a possibility to control the process of oxidation of iron nanoparticles via using a different power of the cold plasma source and different exposition time. This potentiality will be a subject of the next study.

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and J. Pechousek^a (^a*Centre for Nanomaterial Research, Palacky University, Olomouc*, ^b*Department of Experimental Physics, Faculty of Science, Palacky University, Olomouc*):
Use of Cold Plasma for Transformation of Iron Nanoparticles

The pure iron nanoparticles, prepared by a spark discharge were transformed (oxidized) using a cold plasma effect. Structural and size properties of the initial iron nanoparticles as well as final product of iron oxide nanoparticles were characterized using TEM, XRD, BET and Mössbauer spectroscopy.