Preparation and protection of iron and iron compounds

N Koprinarov1,4, M Konstantinova1, G Avdeev2, T Ruskov3 and Tz Tzacheva2

1 Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
2 Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria
3 Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: koprin@phys.bas.bg

Abstract. Iron, iron carbide and iron oxide nano- and micro-particles were synthesized in a hermetically sealed container using ferrocene and a mixture of ferrocene, xylene and water. The particles produced possess well expressed magnetic properties and are wrapped in a protective carbon cover. Carbon provides excellent protection against moisture and chemical influences and insures a long-lasting stability. Structural changes in the particles and their covers were examined at up to 1000 °C in vacuum and 800 °C in air, as were their stability under the influence of acids. The particles morphology was examined by scanning (SEM) and transmission electron microscopy (TEM); their chemical composition and crystal structure were studied by X-ray diffraction (XRD), Mössbauer spectroscopy and electron probe X-ray micro analysis and energy dispersive X-ray spectrometry (EDS).

1. Introduction
Iron is one of the most widely spread elements in nature, as it is a part of the elemental series H, He, C, O, Fe with which the star matter evolves. It forms compounds with a wide spectrum of chemical elements; its compounds with C and O represent a substantial part of this series. Because of its chemical activity under normal conditions on Earth, it cannot be found in a pure form. The good properties of its compounds, however, has made it the most often used metal in practically all industrial sectors and in everyday life, but the problem still remains to be solved of the changes of its properties and those of its compounds under ambient influence. This is especially important in the cases when usage in micro- and nanostructures is intended [1, 2, 3], since the number of atoms on the surface of a very small iron particle becomes commensurate with that in the particle volume. The surface atoms undergo transformation to an unwanted compound, which leads to a drastic change in the particle’s properties. Logically, the idea comes to mind to protect iron and its compounds from contact with the surrounding ambient by depositing a protective coating. This idea is not new [4, 5]. The search for implementation of reliable protection still continues, as no sufficiently good techniques for solving the problem have so far been found. In this respect, carbon seems to be a promising candidate. It is chemically stable when a graphite-type lattice is created and possesses good mechanical properties.

4 To whom any correspondence should be addressed.

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Moreover, when carbon is deposited from a gaseous phase, iron act as a catalyst in the formation of the graphite-type carbon covering on its surface [6 - 9].

The studies presented here were aimed at establishing whether different iron particles can be obtained and coated during the decomposition of carbon and iron containing compounds.

2. Experimental
Ferrocene (Fe(C5H5)2) (Ventron) is used as a source of atoms for forming iron particles. It has the advantage that, when decomposing, except iron atoms it also supplies carbon atoms necessary for the protective coating in even greater numbers than needed. The pyrolytic decomposition proceeds in a stainless steel container (figure 1). Its opening is hermetically sealed by a sphere made also of stainless steel, which is continuously pressed against the container by a hydraulic press thus creating a pressure of 80 MPa inside the container. The temperature of decomposition is reached at a rate of 200 °C/min by heating by a gas burner, while the cooling rate is 30 °C/min. The temperatures of synthesis are within the 300 °C – 600 °C interval and are controlled by a thermocouple mounted in the container wall. The prepared material is studied without any additional treatment. Some of the experiments are carried out with a ferrocene, xylene and water mixture in weight ratio 3:4.5:1 as a starting material. The water is used to stimulate the iron oxidation, while xylene is chosen as an additional source of carbon atoms.

3. Results and discussion
The experiments on pyrolytic decomposition of ferrocene in the temperature interval 300 °C - 600 °C indicate that the temperatures in this interval are sufficiently high for ferrocene decomposition. The XRD spectra of the material obtained demonstrate that the iron and iron compounds prepared differ in composition and structure depending on the synthesis temperature, the process duration and the presence of additional starting substances in the container. For instance, the spectrum of the material prepared at 300 °C confirms the decomposition of ferrocene (figure 2) and the formation of Fe, Fe3C, and Fe2O3. This is supported by Mössbauer spectroscopy of the materials synthesized at 300 °C for different times: 1 min, 5 min, and 30 min (figure 3). The Fe-containing phase ratio

Figure 1. Schematic of the equipment used.

Figure 2. XRD spectrum of the material prepared.

Figure 3. Mössbauer spectra of materials synthesized at 300 °C for: (a) 1 min; (b) 5 min; (c) 30 min.
α-Fe/Fe₃C/superparamagnetic Fe₃C/α-Fe₂O₃ obtained from the Mössbauer spectra is, respectively, 56/25/11/8; 64/21/15/0; 78/11/11/0. One should conclude that the synthesis duration influences not only the material type produced but its quantity as well.

The number of carbon atoms released by the decomposed ferrocene exceeds by a factor of ten that of the iron atoms; when the iron nuclei are of small size, this number is sufficient to cover them by protective coatings [10]. The case of low temperature pyrolysis is similar. The TEM and SEM observations and their analysis indicate that the iron atoms produced by low-temperature ferrocene decomposition (300 °C; 1-5 min) agglomerate and form nuclei of pure iron or of iron compounds covered by carbon (see figure 4a). Because of the small atomic mass of carbon, the carbon layer in the TEM and SEM photos is semitransparent. The number of available carbon atoms rises together with the nucleus size growth when the process lasts longer (20 - 60 min). Conditions appear for growth of carbon nanotubes inside which iron nuclei often remain enclosed (see figure 4b).

The nuclei become larger with morphology typical of magnetite (figure 5a) when the synthesis duration is extended (30 - 60 min) at high temperatures (600 °C - 700 °C) in the presence of xylene and water, as confirmed by the EDS spectra (figure 5b). Under these conditions, only a part of the carbon atoms are spent for the development of coatings. The remaining carbon atoms do not come in contact with the nuclei and build perfect carbon spheres. In the SEM image in figure 5a, the crystallized iron nuclei are seen in white and their carbon coating and the pure carbon spheres are darker.

**Figure 4.** TEM images of material synthesized at low temperature for: (a) 1 min., (b) 30 min.

**Figure 5.** Material synthesized at 600°C:
(a) SEM image;
(b) EDS spectrum.

**Figure 6.** Magnetite crystals: (a) before etching; (b) after etching in HNO₃; (c) after etching in HCl.
The ability of the coatings obtained to protect the iron nuclei was tested by placing the synthesized material in 30% HCl and in 70% HNO₃ at 80 °C. After a 100 hour treatment, no variation in the particle morphology was registered (figure 6). Moreover, no changes in the materials morphology were noticed following thermal treatment at 1000 °C in vacuum and at 600 °C in air.

Conclusions
Experiments with ferrocene pyrolytic decomposition in a hermetically sealed container show that nano- and micro-particles of various morphology and chemical composition can be synthesized. The protective coatings formed are of different types. At low temperatures and a short synthesis process, the iron containing nuclei are small in size and tightly wrapped in a carbon layer. As the temperature and the synthesis duration are increased, carbon starts to form nanotubes using an iron nucleus as a catalyst. In most of the cases, the nucleus remains enclosed inside the tube. At still higher temperatures, besides coating iron nuclei, carbon starts building pure carbon spheres.

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