PREPARATION OF NANOSIZED CARBON BY CHEMICAL LEACHING

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Abstract

Particles of carbon materials with nanosized or nanoporous structure are very prospective in applications for adsorption of gases, vapours and liquids, for cleaning techniques, catalysis and hydrogen storage due to their extremely high specific surface. The research of materials for hydrogen storage is focused on the study of carbon nanostructural materials. Chemical leaching method is one of available methods for preparation of extremely fine carbon powders. Chemical leaching process was used for preparation of the carbon powder by leaching of a cast iron, carbon steel and special alloyed tool steel in hydrochloric acid. Very fine powders were prepared. Powder prepared from carbon steel had highest purity and had amorphous character.

Keywords: carbon powder; chemical leaching; hydrogen storage;

1. INTRODUCTION

Materials with nanostructure or amorphous structure are very requested in various technical branches at the present time. These materials have exceptional properties compared to conventional materials. Special properties of these materials are connected with extremely small size of their structural units. Surface area and surface energy of these materials is rapidly higher, therefore electrical, optical, mechanical and chemical properties are very different from the properties of conventional materials [1]. Metallic and ceramic materials with nanosized structure are already ordinarily used in industrial production. Metallic nanopowders are used in catalysis, electronic, powder metallurgy, pharmacology. Recently, the interest in new nanosized materials has marked progressive tendency [2].

Carbon materials with nanosized or nanoporous microstructure are intensively studied at the present time. Particles of these materials are very prospective in applications for adsorption of gases, vapours and liquids, for cleaning techniques, catalysis and hydrogen storage due to their extremely high specific surface [1,3].

Modern research in automotive industry is focused on utilization of the non-fossil fuel due to a deficiency and a price of the fossil fuel. Another aspect is minimizing of the automotive industry influence on the living environment. Technology of the hydrogen production made great progress hence hydrogen is very prospective alternative fuel for automotive industry. Utilization of the hydrogen for these purposes supposes safe and technologically practicable hydrogen storage. Hydrogen in gaseous or liquid states can be stored only under high pressures. Extremely high mechanical properties of hydrogen reservoirs are required which is connected with high weight of the reservoirs. Therefore the hydrogen storage in solid matter is preferred. Hydrogen can be stored in solid state forming the metal hydrides (MgH2, NaBH4, LiAlH4) or by the hydrogen sorption on the porous particles (Ni, carbon nanostructures). Materials with the low density are preferred for hydrogen storage from practical purposes. The research of materials for hydrogen storage is focused on the study of carbon nanostructural materials. Carbon nanotubes appear to be effective materials for hydrogen storage in solid matter [4].
reinforced composites, reinforcement of armor and other materials, reinforcement of polymer, avionics, collision protection materials, fly wheels are another applications utilizing carbon nanotubes.

Methods for preparation of carbon with nanostructure are based on physical, physicochemical or chemical principles.

**Physical methods** represent laser ablation method, based on the interaction between the laser beam with carbon substrate. Carbon nanotubes and fullerene C₆₀ nanoparticles can be prepared with this technique [5-6]. The influence of arc discharge on graphite can be used for preparation of carbon nanotubes. Carbon nanotubes with high purity can also be prepared by PVD and CVD methods.

CVD method utilizes the **physicochemical principle**. Carbon nanotubes with CVD method are prepared by thermal deposition of preheated gaseous hydrocarbons with presence iron catalyst. Growth of the nanotubes depends on the conditions of the process. Product can be formed by single walled nanotubes or multi walled nanotubes [7-8].

**Chemical methods** can be used for preparation of relatively high amount of nanosized carbon powder. Carbonizing method uses the organic substrate which is pyrolyzed at the high temperature. Process runs at the inert atmosphere (Ar). Product of pyrolysis is carbon with porous structure. Porosity of the product can be influenced by presence of volatile substances (porogens) [9]. Nanocasting method is based on filling the porous precursor (zeolite) by organic liquid, thermal deposition of the organic liquid and removing of precursor by dissolving in HCl+HF. Product is formed by carbon particles. The size and the shape of its particles correspond with pores of used precursor. Nanoporous carbon can be prepared by method using chemical reaction between metal carbides and gaseous chlorine. Microstructure of carbon powder prepared from TiC and SiC is amorphous, carbon prepared from AlC is formed by multi walled nanotubes [10].

Chemical leaching is universal method available for preparation of extremely fine metal, alloy or graphite powders [1,3]. Principle of chemical leaching method consists of several steps. First step is preparation of the binary or the multicomponent alloy. The finer the microstructure of alloy, the finer the particles of prepared powder. Melt spinning method is very effective for preparation ribbons with extremely fine microstructure. Cooling rate achieves the value of 10⁶ Ks⁻¹ [3]. Second step is the dissolution of one or more component of alloy in suitable chemical agent. One or more component remain in the form of the very fine powder. Size and morphology of powder particles depend on the microstructure of alloy used for leaching. Elemental hydrogen is evaluated from the solution during the dissolution of metal matrix. Hydrogen atoms can be bond on the surface of rising powder. Amount of picked-up hydrogen can be indispensable. Chemical leaching method can also be used for preparation of the fine carbon powder. Base alloy used for chemical leaching must contain high carbon content. Cast iron or similar alloys can be used for these purposes.

2. EXPERIMENT

Experiments in this work consist of three sequential steps. First step represents the characterization of materials used for chemical leaching. Alloys with high carbon content were preferred to achieve maximal amount of carbon powder in our experiments. Cast iron, carbon steel and special alloyed tool steel were studied. Chemical composition of these alloys was determined by optical emission spectrometer (GD Profiler 2). Results are in tab 1.
Tab 1: Chemical composition of alloys used for chemical leaching [wt.%]

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>P</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>cast iron</td>
<td>93.01</td>
<td>3.39</td>
<td>2.66</td>
<td>0.52</td>
<td>-</td>
<td>0.10</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>carbon steel</td>
<td>98.20</td>
<td>0.97</td>
<td>0.29</td>
<td>0.34</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>alloyed tool steel</td>
<td>84.24</td>
<td>2.50</td>
<td>3.30</td>
<td>0.46</td>
<td>1.12</td>
<td>-</td>
<td>-</td>
<td>2.20</td>
<td>2.60</td>
<td>2.60</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Microstructures of alloys used in our experiments are documented in Fig.1-3.

![Fig.1.: Microstructure of cast iron](image1)

![Fig.2.: Microstructure of carbon steel](image2)

![Fig.3.: Microstructure of alloyed tool steel](image3)

Carbon is present in cast iron both in the form of graphite lamels and carbides (Fig.1).
Microstructure of carbon steel has hypereutectoid character. Perlite grains are surrounded by cementite network (Fig.2).
Microstructure of special alloyed tool steel is formed by coarse M7C3 carbides in martensite matrix (Fig.3).
Second step of our experiments was chemical leaching of alloys. Chemical leaching was realized with 35% hydrochloric acid at the room temperature for 6 weeks. Powder material was separated from the acid solution by decantation and filtration after chemical leaching. Third step of experiments was the observation of prepared powders. Chemical composition, phase composition and particle size of prepared powders were studied. Chemical composition was determined by Kevex Delta 5 EDS analyzer, phase composition was studied by x-ray spectrometer Philips X’Pert PRO. Particle size of prepared powders was studied by high resolution transmission electron microscope Jeol 3010.

3. RESULTS AND DISCUSSION
Chemical composition of prepared powders is in tab.2. Powders prepared by chemical leaching of three studied alloys were not formed by pure carbon. Powder prepared from carbon steel reached highest purity. Powders prepared from cast iron and carbon steel contained marked amount of the silicon. This fact was expected, because silicon is insoluble in hydrochloric acid. Powder prepared by chemical leaching of alloyed
tool steel contained both high silicon content and high content of chromium, vanadium and niobium. It is due to high stability of chromium, vanadium and niobium carbides in hydrochloric acid. Dissolution of iron from cementite leads to forming of very fine carbon particles.

**Tab.2: Chemical composition of prepared powders [wt.%]**

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>cast iron</td>
<td>70</td>
<td>≤1</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>carbon steel</td>
<td>82</td>
<td>≤1</td>
<td>12</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>alloyed tool steel</td>
<td>28</td>
<td>32</td>
<td>21</td>
<td>14</td>
<td>3</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

Microstructures of prepared powders are in **Fig.4.** Particles with smallest size were observed in powder prepared from carbon steel (lower than 10 nm), the coarsest ones in powder prepared from alloyed tool steel.

**Fig.4:** Microstructure of powder prepared from studied alloys (HRTEM)

Fine microstructure of carbon steel used for chemical leaching was the main presumption for preparation of very fine powder. Some particles in the powder prepared from carbon steel had amorphous character, which is documented in **Fig.5.** There are thin peaks corresponding to crystalline carbon and silicon in the x-ray diffractogram. The wide peak in the spectrum shows the presence of amorphous carbon in the powder.

**Fig.5:** X-ray diffractogram of powder prepared from carbon steel
4. CONCLUSION

Chemical leaching method can be used for preparation carbon powder, which is very interesting material in present time. Purity and morphology of prepared powder depend especially on the microstructure of material used for chemical leaching. The finer the alloy, the finer the prepared powder. Particle size of prepared powders was lower than 10nm. Powder with high purity was prepared by chemical leaching of carbon steel. Some particles of this powder had amorphous character. Alloyed tool steel did not dissolve in hydrochloric acid entirely due to extremely stable metal carbides present in the microstructure of alloy.

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LITERATURE