Phase Formation in Nanocomposites of the C–Pd–Fe System

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Abstract—Metal–carbon nanocomposites consisting of a carbon matrix with dispersed nanosize bimetallic Pd–Fe particles were obtained. It was established that at 500–700°C, the bimetallic particles form a solid solution of iron in palladium. It was concluded that raising the intensity of infrared pyrolysis to 800–1100°C leads to the formation of intermetallic compounds whose composition depends on the temperature of nanocomposite fabrication.

Keywords: nanocomposites, catalysts, pyrolysis, intermetallic compounds.

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INTRODUCTION

As of late, researchers have devoted much attention to elaborating the principles of obtaining metal-containing nanocomposites, a new class of functional materials having a wide variety of potential uses. An important application of nanocomposites based on carbon and nanoparticles of precious metals is their use as catalysts in chemical and petrochemical processes [1].

A fundamental problem whose solution opens the possibility of controlling the structure of nanocomposites and thus their properties is studying the dependence of the sizes of metallic nanoparticles and the structural characteristics and functional properties of metal–carbon nanocomposites on the conditions of their fabrication [2].

This work is devoted to studying the process of phase formation in metal–carbon nanocomposites.

EXPERIMENTAL

Metal–carbon composites were obtained under the conditions of infrared (IR) pyrolysis of a precursor based on polyacrylonitrile (PAN) and palladium and iron compounds.

PAN was synthesized using an oxidation—reduction catalytic system, following the method in [3]. The precursor was prepared via the joint dissolution of PAN and PdCl2 (Aldrich, 99%) or FeCl3 (Aldrich, 99%) in dimethylformamide (DMF, Fluka, 99.5%).

Pyrolysis was performed in the IR chamber of a pulsed photon annealing setup. IR annealing was performed in a two-stage mode: preliminary annealing in

Fig. 1. Reflection peaks from the (111) plane of the palladium fcc phase in samples obtained at (a) 500 and (b) 1100°C, where 1 is the Pd phase, 2 is the Pd3Fe phase, and 3 is the PdFe phase.
air at 150 and 200°С for 15 min each, during which the solvent was removed and the initial structurization of PAN was performed, and primary annealing in an inert atmosphere at the required intensity of IR radiation, which varied from 500 to 1100°С. The time of primary annealing was 2 min. Microphotographs of the samples were taken on a LEO912 AB OMEGA X-ray electron microscope.

The phase and structural studies were performed at a temperature of around ~20°C on a Rigaku X-ray diffractometer with Bragg–Brentano focusing for FeKα radiation in the continuous mode. The experimental results were processed by approximation and Fourier-analysis [4]. The distribution of the diameters of spherical crystallites was calculated from the X-ray diffraction data in [5] as well.

RESULTS AND DISCUSSION

The lines of the metallic palladium phase and those of the carbon phase are present in the diffractograms of all samples. At a pyrolysis temperature of 500–900°С they are an amorphous halo; at 1000–1100°С, they form an asymmetric washed-out intensity peak with a maximum in the field of graphite angles.

The reflection peaks from plane (111) of the palladium face-centered cubic (FCC) phase in the studied samples are given in Fig. 1. Figure 1 also shows the position of the most intense maxima of the Pd, Pd3Fe, and PdFe phases, which measure 51.12°, 51.81°, and 52.35° on the 2θ scale, respectively.

The diffraction lines are symmetrical at a pyrolysis temperature of 500–700°С. The peaks exhibit shoulders in the field of smaller and larger angles, and they broaden with an increase in synthesis temperature. The maxima of the intensity of the sample obtained at 800°С are particularly nonequilibrium in character. The diffraction lines shift to the region of larger angles with an increase in the pyrolysis temperature. They clearly exhibit a shoulder on the side of larger angles.

The results from calculating the lattice periods are given in Table 1. We can see that the lattice period decreases with an increase in the intensity of IR radiation.

The processes of carbonization leading to the formation of a carbon matrix take place in PAN under the action of noncoherent IR radiation. The reflections from this phase in the samples synthesized at a temperature of 500–900°С form an amorphous halo at angles of 20° to 40°. In the case of the samples obtained upon IR pyrolysis at 1000 and 1100°С, a reflection peak appears at the reflection angles corresponding to graphite. This peak is of low intensity, and is strongly smeared out and asymmetric in the region of small angles. All of the above indicates the appearance of graphite-like structures in the samples.

It was shown by means of X-ray electron microscopy that the metallic inclusions are homogeneously distributed over the volume of the sample. The metal particles are close to spherical in form. The size of the metallic inclusions varies over a rather broad interval: both a very fine fraction with a particle size of several nanometers and large particles with diameters of 50–100 nm are observed in the samples. As an example, a microphotograph of the sample of the C–Pd–Fe system obtained at a pyrolysis temperature of 1100°С is shown in Fig. 2.

Histograms of the size distribution of the fine fraction of the metallic phase were constructed on the basis of microphotographs and are shown in Fig. 3. The sample obtained at a pyrolysis temperature of 700°C has small particle sizes in the interval of 1.5 to 15 nm. We observe a sharper fraction differentiation of the metallic inclusions upon an increase in the synthesis temperature. The fine fraction of the metallic parti-

<table>
<thead>
<tr>
<th>T, °C</th>
<th>l, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.38762</td>
</tr>
<tr>
<td>600</td>
<td>0.38528</td>
</tr>
<tr>
<td>700</td>
<td>0.38502</td>
</tr>
<tr>
<td>800</td>
<td>0.38278</td>
</tr>
<tr>
<td>900</td>
<td>0.38041</td>
</tr>
<tr>
<td>1000</td>
<td>0.38041</td>
</tr>
<tr>
<td>1100</td>
<td>0.38006</td>
</tr>
</tbody>
</table>

Note: T is the pyrolysis temperature, l is the lattice period.