# FORMATION OF ORDERED CARBON NANOSTRUCTURES AT PYROLYSIS OF HYDRATED CELLULOSE CONTAINING THE METALS OF FERROUS SUBGROUP

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## Introduction

The metals of ferrous subgroup and their alloys are usually used as the catalysts in processes of formation ordered carbon nanostructures [1]. There is a clear correlation between the sizes of catalyst particles and the tipe of carbonic deposits on their surface.

It is known many ways for obtaining of catalytic nanosize systems. The pyrolysis of systems *polymer - salt* is one of them. During this process the salts are reduced up to free highly dispersed metal particles. These particles are then the catalysts of process of carbon nanostructures formation.

At the present work the process of carbon structuring is studied at carbonization in temperature of heat treatment (THT) 400-900 $^0$C of hydrated cellulose (HC) fibres, impregnated by the salts of metals of ferrous subgroup, that was resulting to formation of metalcarbon fibres (Me-CF).

## Results and discussion

The conditions of carbonization, and also the methods of thermal, electron microscopy, IR and X-ray diffraction researches are described in [2].

It is established, that during the carbonization of systems *HC- salt of metal of ferrous subgroup* the reducing of the salts to the free metals take place. These highly dispersive metals catalyze (at definite THT) the processes of carbon structuring with formation of different phases of ordered carbon. On literary data [3], the different mechanisms of the growth of ordered carbon nanostructures on the surface of metallic catalysts are characterized by three common stages: the dissolving of carbon in metal, the formation of carbon nucleating centre on the surface of metal particle and the growth of carbon nucleating centre resulting in to formation of different carbon products. The size of the carbon nucleating centre determines the sizes of carbon deposits formed on the surface of the catalytic particles. So, at the large sizes of a critical nucleating centre (radius $r > 10\text{-}20$ nm) the extented carbon layers are formed, which capsulate the metal particles, and/ or the carbon nanofibers are obtained. When the small-size multiple nucleating centres ($r \approx 0{,}35\text{-}1{,}5$ nm) are arised on a metal surface, the bundles of single-layer carbon nanotubes are formed. In the case of the intermediate sizes of a critical nucleating centre there is a formation of more or less ordered coaxial cylindrical structures, including multilayer carbon nanotubes. In our case on the base of the data of electronmicroscopy and X-ray diffraction analysis (table 1) it is possible to conclude, that on a surface of metal particles in the structure of Me-CF the turbostrate carbon with $d_{002} = 0{,}344$ nm and graphitic nanofibers with $d_{002}=0{,}337$ nm are formed, the dimentions of the areas of coherent diffraction (ACD) on the axis *c* and *a* are 6,3 nm ($L_c$) and 22,8 nm ($L_a$) accordingly. In addition that the capability of the formation of other carbon nanostructures is not excepted.

At the work it is established that the morphological and crystallographic characteristics of the formed nanostructures and also the initial temperature of their formation depend on the conditions of Me-CF obtaining and cationic-anionic structure of the salt additions introduced into the initial HC fibers. So, at the pyrolysis of HC with the additions of ferric and cobalt chlorides the carbon structuring does not occur: amorphous carbon are formed in all studied interval of THT.

The formation of structure ordered carbon phases with $d_{002}=0{,}344$; 0,337 nm take place at pyrolysis of HC with the additions of $NiCl_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$ and $Fe(NO_3)_3$. The temperature of begining of the structuring for each system is various. So, in a system HC-Fe $(NO_3)_3$ the appearance of the carbon ordered phases take place at THT 600 $^0$C, in systems HC-$Ni(NO_3)_2$ and

HC- $NiCl_2$ - at 800 $^0$C, in a system HC-Co $(NO_3)_2$ - at 900 $^0$C.

The appearance of new phases of structure ordered carbon is accompanied by the fall of Me-CF strength and by the development of a porosity. The sorbate volume of pores in the samples of Me-CF with THT above 800 $^0$C, which was determined by the sorption of benzene, makes 0.13-0.16 см$^3$·g$^{-1}$ for chlorides and 0.11-0.26 см$^3$·g$^{-1}$ for nitrates.

The availability of highly dispersive metals and developed specific surface in the structure of Me-CF opens the capabilities for usage of Me-CF as active catalysts of chemical processes, including the processes for obtaining of nanostructured carbon.

## Conclusions

The catalytic influence of metals of the ferrous subgroup on the process of carbon structuring in carbonised HC is established. The influence of anionic structure of introduced salts on the process of the HC thermal decomposition and following transformations in the system *metal - carbonic rest* are shown. The obtained results present both scientific and practical concern at creation of catalysts for obtaining of nanostructured carbon.

## References

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Table 1. Relation of change of intensity (I), interplanar spacing interval ($d_{002}$), medium dimentions of ACD ($L_c$, $L_a$) for coal rest obtained after heat treatment of hydrated cellulose with the additions of the metal salts of ferrous subgroup

| Sample | THT, $^0$C | I, Arb.un. | $d_{002}$, nm | $L_c$, nm | $L_a$, nm | I, Arb.un. | $d_{002}$, nm | $L_c$, nm | $L_a$, nm |
|---|---|---|---|---|---|---|---|---|---|
| | | The first component | | | | The second component | | | |
| HC | 800 | | | | | 41 | 0.386 | 1.0 | 3.6 |
| HC -$Fe(NO_3)_3$ | 600 | 26 | 0.337 | 6.3 | 22.7 | 14 | | 2.9 | 10.4 |
| HC - $Fe(NO_3)_3$ | 800 | 56 | 0.337 | 6.3 | 22.7 | 16 | 0.344 | 2.2 | 7.9 |
| HC -$FeCI_3$ | 600 | | | | | A broad halo | | | |
| HC -$FeCI_3$ | 800 | | | | | 30 | 0.386 | 1.1 | 3.9 |
| HC -$Co(NO_3)_2$ | 600 | | | | | Amorphous | | | |
| HC -$Co(NO_3)_2$ | 900 | 18 | 0.337 | 6.3 | 22.8 | 16 | 0.344 | 1.1 | 3.2 |
| HC -$CoCI_2$ | 600 | | | | | Amorphous | | | |
| HC -$CoCI_2$ | 800 | | | | | Amorphous | | | |
| HC -$Ni(NO_3)_2$ | 600 | | | | | Amorphous | | | |
| HC -$Ni(NO_3)_2$ | 800 | 28 | 0.337 | 6.3 | 22.8 | A broad halo | | | |
| HC -$NiCI_2$ | 600 | | | | | A broad halo | | | |
| HC -$NiCI_2$ | 800 | 92 | 0.344 | 7.8 | 28.1 | 15 | 0.344 | 2.9 | 10.4 |