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PREPARATION OF METAL-CONTAINING NANOSTRUCTURES IN NANOREACTORS OF POLYMER MATRICES.

Abstract: With an increase in the nickel content in the nanoreactor, the formation of nanotubes is observed. In contrast to PVA gels, in complex gels containing PEPA there is an increase in reduced nickel coordinated to the C=C bond during the process

Key words: PVA, PVA–PEPA–AA, PVA–PEPA, carbon nickel-containing nanostructures.

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ПОЛУЧЕНИЕ МЕТАЛЛОСОДЕРЖАЩИХ НАНОСТРУКТУР В НАНОРЕАКТОРАХ ИЗ ПОЛИМЕРНЫХ МАТРИЦ.

Аннотация: С увеличением содержания никеля в нанореакторе наблюдается образование нанотрубок. В отличие от гелей ПВА, в сложных гелях, содержащих ПЭПА, в процессе процесса происходит увеличение восстановленного никеля, координированного по связи C=C.

Ключевые слова: ПВС, ПВС-ПЭПА-АА, ПВС-ПЭПА, углеродные никельсодержащие наноструктуры.

Introduction

Polymer matrices from PVA, PVA–PEPA, PVA–PEPA–AA were prepared by mixing solutions of the corresponding components according to the method described in [1,2]. Then the gels formed during drying were treated with solutions of metal chlorides (Co, Ni, Cu). According to the IR spectra, the interaction of metal ions, for example, nickel, with the oxygen of hydroxyl and ketone groups, as well as with the nitrogen of amine groups, was detected in the resulting colored films. In this case, in the case of using nickel chloride, the coordination number of Ni_2+ in PVA gels is 4, and in PVA–PEPA and PVA–PEPA–AA gels it corresponds to 6. With subsequent thermal exposure (stepwise heating to 400ºC), the color of the film changes to black color with the formation of a porous intermediate product, which was washed and dispersed, followed by isolation and drying of the nanoproduct. In this case, the formation of nanostructures is a redox process, which involves the reduction of the metal and carbonization of the organic components that form the walls of the nanoreactor.

X-ray electron study was carried out using C 1s and Ni 3p spectra nanoproducts obtained from $NiCl_2$ and PVA, PVA–PEPA, PVA– gels PEPA-AA [3]. The Ni 3p spectrum has a complex shape due to the presence of several nickel compounds and the imposition of a multiplet structure, the shape of which depends on the valency of the metals. For example, calculations of the multiplet structure due to the interaction of 3p–3d unfilled shells in nickel complexes for 3d8 showed that the spectrum of Ni 3p consists of three intense maxima: the main maximum and two more at a distance from the main peak, 2.5 eV and 5.0 eV, as well as a weakly intense series of peaks at a distance of 10eV [2]. The results of X-ray electron studies of the samples are given in the table.

Table 1 . Relative content of Ni and C in the studied samples

No.	Compound sample	Ratios connections carbon C1s	Ratios connections nickel Ni3p
1	2PVA+1$NiCl_2$	CC(^{sp2}):CH:CO = (50:40:10)%	Ni-O(H) : Ni-Cl = (55:45)%
2	1PVS+1PEPA+1 $NiCl_2$ _	Ni-C:CC(^{sp2}):CC (^{sp3}):CH= (21:42:11:26)%	Ni-C:Ni(N^+):Ni-Cl = (12:35:53)%

3	2PVS+2PEPA+1 NiCl2 _	Ni-C:CC (^{sp2}):CC (^{sp3}) :CH= (15:28:14:43)%	Ni-C:Ni (N $^{+}$):Ni-Cl = (23:50 :27)%
4	1AA+2PVS+ +2PEPA+1NiCl $_{2}$	Ni-C : CC (^{sp2}):CC(^{sp3}) :CH= (10:39:11:40)%	Ni-WITH:Ni(N $^{+}$) = (33:67)%

X-ray electron studies of the C1s spectrum of the nanoproduct obtained from the 2PVA–NiCl2 mixture showed the presence of a C–C bond with sp2 hybridization of valence electrons, i.e. similar to graphite, as evidenced by the satellite structure at 306 eV, as well as the presence of hydrocarbons and carbon-oxygen CO bonds. CC connection with sp3 is weakly detected by hybridization for this mixture. The O1s spectrum indicates the presence of adsorbed and bound oxygen. All these components are in a percentage ratio of 50:40:10 (Analysis of the chemical shifts of the Ni 3p spectrum indicates the presence of a nickel bond Ni-O or Ni-O(H), as well as Ni-Cl or (H)O–Ni–Cl approximately in the same percentage. There are no reduced Ni atoms in the analyzed layer. However, in accordance with the data of X-ray diffraction analysis, electron diffraction (ED) and transmission electron microscopy (TEM), there are tubular multilayer nanostructures that form dense bundles (“intergrowths”) [4]. This is also indicated by the presence in the spectra of carbon of a C-C bond with sp2 hybridization of the valence electrons of carbon. Transmission electron microscopy micrographs show that the resulting carbon films roll up, forming “scrolls.” It is possible that the side surfaces of such nanostructures are active enough for intergrowths to form The moment of nanofilm folding, as well as the result of the process - intergrowths of tubulenes, are shown in Fig. 2.

The C1s spectrum of a nanoproduct obtained from a mixture containing PVA, PEPA and $NiCl_2$ in a 1:1:1 ratio contains the following components: Ni–C interactions; C–C bonds with sp2 hybridization of carbon valence electrons; C–C bonds with sp3 hybridization of carbon valence electrons, as well as C–H bonds.

The listed components are in the following percentages ratio: Ni-C:CC (sp2):CC (sp3):CH = 21:42:11:26. The peak in the O 1s spectrum is so small in contrast that the content of bound oxygen with carbon is taken to be zero.

Analysis of the Ni $_3$ p spectrum showed the presence of Ni-C (12%), Ni(N+) (53%) and Ni-Cl (35%) in the nanoproduct. A comparison of the results of IR spectra and X-ray electron spectra of N1s indicates the presence in the nanoproduct of =N+= groups with an electronegativity of [4], which explains the corresponding chemical shift in the Ni3p spectrum. The formation of = N+ = groups was noted when studying the IR spectra of the obtained color films (xerogels), as evidenced by bands in the regions 2280–2130 cm^{-1} and 1710–1570 cm^{-1} [5]. At the same time, bands attributed to C=N and N=N bonds were detected in the spectra. From the analysis of the spectra, one can conclude that conjugation chains are formed, which indicates the possibility of the formation of a thermostable coordination polymer with the participation of nickel atoms. In this case, the coordination number of nickel, by analogy with inorganic analogues, can take the value 6.

The presence of bonds with C–C sp2 and C–C sp3 hybridization of carbon valence electrons in a ratio of 2:1 indicates the presence of nanotubes, but since there are more C–C bonds with sp2 hybridization, it can be assumed that there are graphite inclusions, which arise due to the formation of the crystalline phase of the precursor polymer. This Microscopic studies also confirm this. Can

suggest that the presence of PEPA in the mixture leads to the reduction of nickel, partially oriented to carbon, and to an increase in the likelihood of nanofilm ruptures at phase boundaries with the formation of smaller single-layer nanostructures of small diameter. This can be illustrated by transmission electron microscopy data (Fig. 5). The micrograph shows nanotubes with a diameter of about 10 nm and a length of approximately 200 nm against the background of amorphous thin “crumpled” nanofilms and small particles of graphite with metal-containing nanocrystals.

With an increase in the content of the polymer phase and a decrease in the $NiCl_2$ content (Table 1) in the C1s spectrum of the nanoproduct obtained from the 2PVA–2PEPA–$NiCl_2$ mixture, the ratio of components changed as follows: Ni-C : CC (sp2):CC (sp3):CH = 15: 28:14:43.

Analysis of the Ni3p spectrum showed the presence of Ni (Ni-C) in the sample and the presence of Ni(N+) interactions in the ratio Ni-C:Ni(N+): Ni-Cl = 23:50:27, which indicates the coordination of nickel with positively charged nitrogen . In this case, the amount of interacting nitrogen significantly prevails over the possible oxygen present in the nanoproduct. A decrease in the content of nickel ions in the initial composition changed the nature of the coordination interaction, which increased the reduction of nickel and caused an increase in the content of the heat-resistant polymer phase.

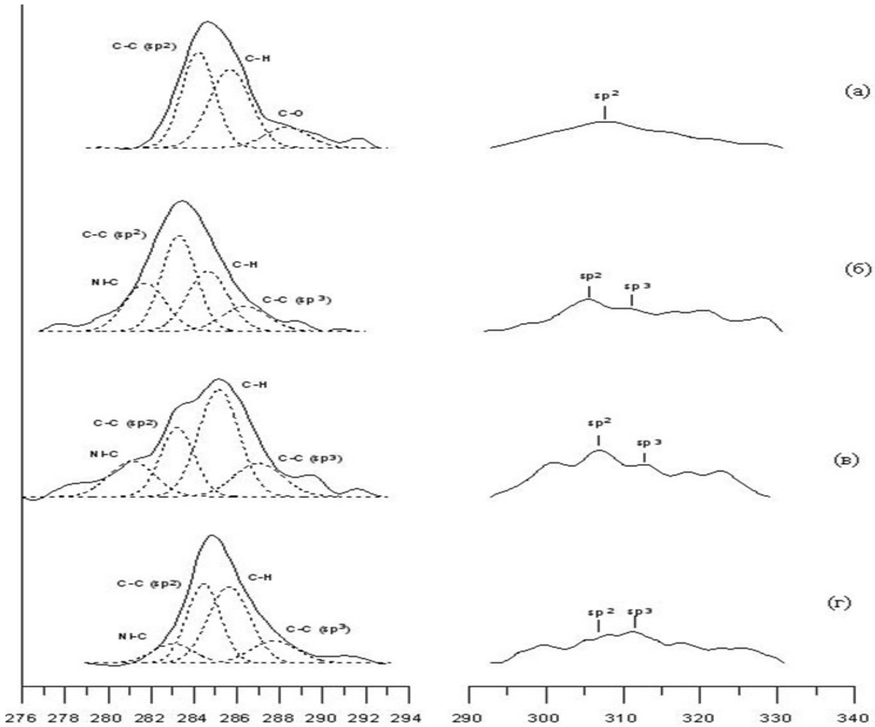
The ratio of satellites reflecting sp2 and sp3 hybridization decreased.

Therefore, it can be argued that the content of small single-walled nanotubes has increased. Moreover, judging by transmission electron microscopy (TEM) and electron diffraction (ED) data, graphite inclusions and an abundance of small tubular nanostructures were noted. This fact can be explained by the formation of a more stable crystalline polymer phase with increasing PEPA content.

During the formation of nanostructures in PVA-PEPA-AA gel nanoreactors, the ratio of satellites increased, apparently due to a change in the mechanism of coordination of nickel with nitrogen and oxygen located in the walls of the nanoreactors. Therefore, the proportion of the hydrocarbon part of the heat-resistant polymer phase increased and the content of reduced nickel saturated with carbon decreased slightly, because There is an increase in stress during thermal exposure and the catalytic process in the resulting nanofilms, followed by their ruptures and the folding of pieces of amorphous sections of the films under the influence of nickel ions or atoms. A variant of nanofilm folding is shown in a transmission electron micrograph (Fig. 3.5.4).

The following components were found in the C1s spectrum: Ni(C):C–C(sp2):C–C(sp3):C–H = 10:39:11:40. Based on the ratio of the components C–C(sp2) and C–C(sp3), one can judge the shape and size of the resulting nanostructures. TEM and ED data confirm the presence of graphite films in the sample and an increase

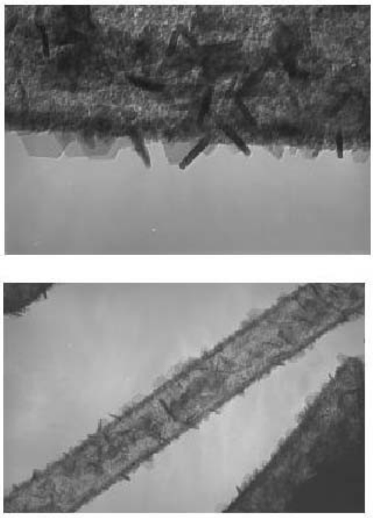
diameter of nanostructures, which correlates with XPS data (the contribution decreased component with sp3 hybridization). In addition, there are some “intergrowths” of nanostructures, which explains the increase in satellite attributed to sp2 hybridization. Analysis of the Ni3p spectrum showed the presence of reduced nickel (Ni-C and Ni(N+) interactions in a ratio of 33:67.



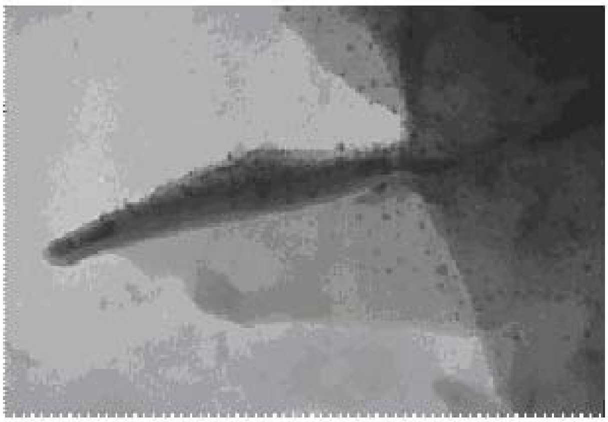
Rice. 1. X-ray electron C1s spectra samples, manufactured from the following mixtures: A) 2PVA+1$NiCl_2$; b) 1PVA+1PEPA+1$NiCl_2$; V) 2PVA+2PEPA+1$NiCl_2$; G) 1AA+2PVA+2PEPA+1$NiCl_2$

X-ray electron C1s spectra of samples made from the following mixtures: a) 2PVA+1NiCl2; b) 1PVA+1PEPA+1NiCl2; c) 2PVA+2PEPA+1NiCl2; d) 1AA+2PVA+2PEPA+1NiCl2;

Rice. 3. Microphotograph obtained using TEM and reflecting the moment of nanofilm folding and the formed intergrowths



Rice. 4. Microphotographs obtained using TEM and reflecting the formation of small nanotubes and nickel nanocrystals on nanofilms and nanoribbons;



Rice. 5. Microphotograph obtained using TEM and reflecting the moment of folding of a nanofilm with small formations of graphene and nickel nanocrystals.

Based on the results of X-ray electron studies and TEM, ED, and IR data, we can assume the following model for the formation of carbon nickel-containing nanostructures:

The formation of carbon nanotubes or tubulenes containing nickel nanoclusters, in some cases nickel nanocrystals, occurs during a redox process in which nickel compounds act as the oxidizing agent, and hydrocarbon or amine groups are the reducing agents.

During the process, chlorine and oxygen are removed from the sphere of interactions, carbonization occurs with the formation of corresponding nanostructures. In this case, amorphous nanofilms are first formed, which are rolled up into cylindrical nanostructures of a certain diameter. In the case of using nanoreactors in the PVA gel, multilayer tubulenes are formed, which are prone to the formation of “intergrowths”, which determines the presence of C–C bonds with sp2 hybridization.

The formation of gels of complex composition, including polyethylene polyamine or polyethylene polyamine and acetylacetone, leads to acceleration of the processes of metal reduction and partial oxidation of the hydrocarbon part of the organic phase. The formation of crystalline phases in a carbon nanofilm is accompanied by an increase in internal stresses and ruptures of the nanofilm with the release of its amorphous part. Pieces of amorphous parts of the film roll up into “scrolls” or form shells of nanocrystals nickel Based on the results obtained, the following conclusions can be drawn:

1. In contrast to PVA gels, in complex gels containing PEPA there is an increase in reduced nickel coordinated to the C=C bond during the process.
2. With increasing nickel content in the nanoreactor, the formation of nanotubes is observed.
3. Adding AA to PVA and PEPA increases the content of graphite inclusions, but does not reduce the content of the coordination polymer.

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