



Carbon'02 **in** Beijing

**An International Conference on Carbon
15-19 September 2002 Beijing, CHINA**

SHANXI CHUNQIU AUDIO-VISUAL PRESS
ISBN 7-900362-03-7/G.03

Welcome

Foreword

Plenary Lecture

Oral Sessions

Poster Sessions

Author Index

Keyword Index

Sponsors

Awards

Organization

Instruction

CARBON '02



An International Conference on Carbon
September 15-20, 2002 Beijing, China

XPS STUDIES OF GRAPHITE COMPOUNDS WITH OXYGEN, FLUORINE AND PENTAFLUORIDES

Yu.M. Nikolenko and A.M. Ziatdinov*

*Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences
159, Prospect 100-letiya, 690022 Vladivostok, Russia*

Abstract - We have studied by the X-ray photoelectron spectroscopy graphite compounds with oxygen, fluorine, NbF₅, MoF₅, TaF₅, SbF₅ and, for comparison, the samples of fluorinated lignin. In F1s spectra of fluorinated graphite oxides and fluorinated lignin was found a peak with the value of binding energies being intermediate between values in a typical ionic compound LiF and covalent compounds of type (CF)_n and -(CF₂-CF₂)_n-. The substances under study, even at high oxidizer content at all synthesis stages contain structure fragments with carbon having sp²-hybridized orbitals of the valent electrons. The bond formed between fluorine and these fragments is of semi-ionic type at the used method of fluorination. The temperature which allows the semi-ionic fluorine-carbon bond formation in the investigated compounds is found to be below 100°C. The observation of semi-ionic state of fluorine in the fluorinated lignin allows to assume that the extended lamellar structure of initial substance is not necessary for the formation of semi-ionic bond between fluorine and carbon. In all penta-fluoride graphite intercalation compounds the F1s spectra consist of a single peak. In graphite intercalation compounds with NbF₅ and TaF₅ the C1s spectra consist of two peaks. In the Me3d spectra of all compounds investigated the peaks corresponding to MeF₃ molecules was not observed. Basing on the XPS data the model of electronic structure was proposed for compounds investigated.

Keywords: A. intercalation compounds; B. x-ray photoelectron spectroscopy; D. electronic structure.

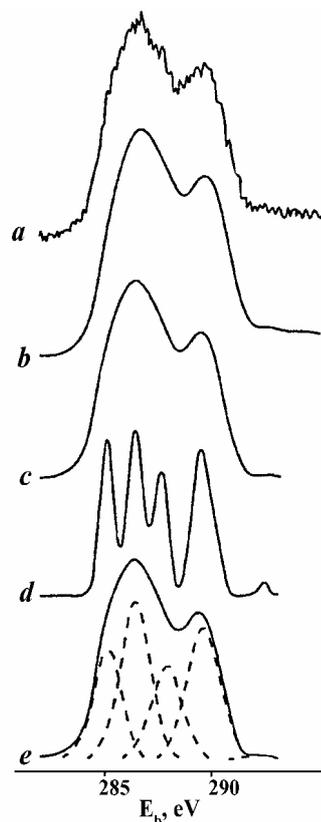
1. INTRODUCTION

The possibility of practical applications and versatility of properties of fluorinated carbon systems maintain interest to their electronic structure and bond type between a carbon matrix and fluorine, structure of guest molecules layers. The structure, bond type and physical properties of the final product of the fluorinated carbon synthesis depend on the synthesis condition, reagents and host matrix structure.

Moran M.J. *et al.* [1] analyzed the intercalated graphite with AsF₅ and reported that the reaction of disproportionation took place and AsF₃ and AsF₆⁻ formed. Wortmann G. *et al.* [2] reported that in some cases the intercalated layers may be present as polymerized macromolecules with common negative charge.

Previous X-ray photoelectron spectroscopy investigations of fluorinated carbon fibres (FCF) [3] have shown the possibility of semi-ionic carbon-fluorine bonds. X-ray photoelectron spectra of graphite fluoride C₂F (GF) prepared from graphite-BrF₃ provide evidence for a semi-ionic C-F bond [4]. These fluorinated carbon systems were synthesized at temperatures below 100°C and the starting substances had a layered graphite matrix with unsaturated C-C bonds which define the possibility for semi-ionic carbon-fluorine bond formation [5, 6]. In Ref. [7], the influence of the degree of graphitization of initial matrix on fluorination process and on bond type between carbon and fluorine has shown. Koh M. *et al.* [8] reported that modification of electron structure of graphene layers in C_xN by nitrogen substitution may enhance the reactivity of compound with fluorine.

In this work the results of the X-ray photoelectron spectroscopy (XPS) study of graphite intercalation



compounds (GIC) with metal pentafluorides NbF₅, TaF₅, SbF₅, MoF₅ and fluorinated graphite oxides (FGO) are present. The XPS spectra of fluorinated lignin (FL) were also measured to

Fig. 1. The example of treatment of the experimental XPS spectrum by computer: C1s spectrum of the FGO No. 8 "B". a) Actual spectrum, b-d) stages of computer processing (see text), e) results of computer simulation.

estimate the necessity of an extended layered structure in the initial substances to obtain the compounds with semi-ionic bonds between fluorine and carbon. FGO and FL were synthesized at temperature range when the formation of semi-ionic bond between carbon and fluorine usually observed.

*Corresponding author: E-mail address: chemi@online.ru; Fax: +7-4232-311889

2. EXPERIMENTAL

Graphite intercalated compounds C_xMeF_5 (Me=Nb, Ta, Sb, Mo, etc.) are well known representatives of the wide family of synthetic metals. GICs studied $C_{22}NbF_5$, $C_{13}TaF_5$, C_xSbF_5 , C_8MoF_5 were synthesized from the gas phases of the corresponding pentafluorides. Synthesis of the NbF_5 and TaF_5 was made by fluorination of corresponding metals by elemental fluorine at the reactor temperature 200–500°C. The MoF_5 was prepared by fluorination of metal wire heated up to 500°C in the stream of elemental fluorine cooled down to –190°C. Standard compound SbF_5 was used for synthesis of C_xSbF_5 . GICs with the Nb, Ta, Sb and Mo pentafluorides are synthesized by exposition of high oriented pyrolytic graphite (HOPG) plates during a month over the melted pentafluorides at temperatures which were on 10° C higher than the melting temperatures of the clear pentafluorides.

To synthesize the FGO we used the graphite oxides (GO) with different oxygen contents. The starting graphite oxide (GO) series was synthesized using $KMnO_4$ mixed with 96% sulphuric acid and 68% nitric acid as an oxidizing agent. The amount of the oxidizing agent was increased in steps to prepare a series of thirteen samples. In this series the ratio of the carbon to the oxygen (C/O) in the final products changes from 10.2 to 1.5 (see Table I). Different oxygen contents lead to the different degree of modification of the starting graphite electronic structure.

All GO samples obtained were fluorinated under identical conditions with a large excess of BrF_3 at room temperature. The hydrolysis of the BrF_3 solvated in the oxidized matrix is accompanied by additional oxidation and fluorination of the starting product, and this strongly loosens the structure and produces a more finely dispersed compound. By collecting the latter on a separating funnel, the hydrolysis product was divided into a hydrophobic phase (light, “L”) and a hydrophilic phase (bottom, “B”) with different oxygen-fluorine ratios. The hydrophobic phase came to the solution surface, but the hydrophilic phase sank to the bottom of the solution. The method employed in synthesizing the compounds studied here is described in greater detail in Ref. [9]. Both the phases were investigated by XPS.

Hydrolyzed lignin was used to synthesize the fluorinated lignin (FL). Hydrolysed lignin is polymer with branched macromolecules and configurational irregularity. It is amorphous yellow-brown substance with molecular mass varies from 10^2 up to 10^6 . Fluorination of lignin was carried out with BrF_3 in a hydrogen fluoride atmosphere over the temperature range –13°C to –3°C. The product obtained was washed with hydrogen fluoride. Excess of hydrogen fluoride was removed in vacuum at 27°C.

The investigation of the C_xMeF_5 , GO, FGO and FL was run with a standard ES 2401 spectrometer using AlK_{α} radiation. The resolution at the gold $4f_{7/2}$ peak was 1.5 eV. During the measurements, the vacuum in the analyser chamber was maintained at 6×10^{-8} mm Hg. In the experiments with the C_xMeF_5 the dry box was used to decrease the contact of the samples with the atmosphere water. The box was connected with the spectrometer chamber for preparation of the samples.

In Refs. [1, 10] was reported that the chemical shift for C1s-electrons in intercalated compounds lies in the range of experimental results reproduction (≈ 0.2 eV). In our XPS experiments with C_xMeF_5 we used the binding energy (E_b) of the C1s-electrons for $C_{8.2}SbF_5$ which was measured in Ref. [11] and is equal to 284.3 eV. In XPS experiments

with the GO and FGO the spectrometer energy scale was calibrated against the C1s peak of the carbon contaminations, whose binding energy was taken to be 285.0 eV. For determination of the fluorine chemical state in the FGO we also measured the values of the fluorine modified Auger parameter α' . This parameter is defined as the sum of measured binding energy of F1s and kinetic energy of $KL_{23}L_{23}$ fluorine Auger line and does not depends on spectrometer energy scale calibration.

The correlation function that allows for different spectral yields of the C1s and F1s photoelectrons was found experimentally for the standard compounds $(CF)_n$ and $(C_2F_4)_n$. The relative concentrations of the other elements were determined using the photo-ionization cross-section values from Ref. [12]. The influence exerted on the measurements by the different weakenings of the C1s and F1s electron flows in the contaminated surface layer was judged from the change in the ratio between the intensities of the matrix fluorine and carbon lines before and after gold was sputtered onto the sample surface, using the bottom phase of compound No. 6 as an example. This sputtering was carried out in the spectrometer chamber for preparation of the samples.

To obtain more information the spectra were treated by computer. The sequence of operations in processing the C1s electron spectra of FGO No. 8 “B” is exemplified in Fig. 1. The processing of the spectra consists of two steps. 1) Statistical noise filtration (Fig.1b), background subtraction, satellite structure that results from nonmonochromaticity of the X-ray source subtraction (Fig.1c). 2) the quantities of the components and their positions in the complex C1s electron spectra of the FGO, FL samples and in the spectra of some GO compounds were roughly estimated by processing the spectra by the method suggested in Refs. [13, 14] (Fig.1d). The processed spectra are equivalent to spectra recorded on an instrument with a linear characteristic and a resolution two times higher than that of the real experiments. Next, after first step of the treatment GO and FGO spectra were simulated from components which have, respectively, different and Gaussian line shapes. In selecting the shape of the lines that are the components of the spectrum of the carbon for the GO series, we also used the approach described in Ref. [15].

3. RESULTS AND DISCUSSION

Some experimental results of our XPS investigation of C_xMeF_5 samples are present bellow.

$C_{22}NbF_5$. The C1s spectrum consists of two peaks with the binding energies $E_b=284.3 \pm 0.1$ eV and 285.5 ± 0.1 eV (Fig. 2a, left). The F1s spectrum consists of a single peak with the binding energy $E_b=684.7 \pm 0.1$ eV (Fig. 2a, right). The Nb3d electrons give rise to spin-doublet peaks with the energies 208.3 ± 0.1 and 210.8 ± 0.1 eV.

$C_{13}TaF_5$. The C1s spectrum consists of two peaks with the binding energies $E_b=284.3 \pm 0.1$ eV and 286.4 ± 0.1 eV (Fig. 2b, left). The F1s spectrum consists of a single peak with the binding energy $E_b=685.5 \pm 0.1$ eV (Fig. 2b, right). The Ta4f spin-doublet peaks have the energies 28.1 ± 0.1 and 29.6 ± 0.1 eV.

C_xSbF_5 . The C1s and spectra consists of single peaks with the binding energies $E_b=284.3 \pm 0.1$ eV (Fig. 2c, left). The F1s spectrum consists of a broad single peak with $E_b=686.0 \pm 0.1$ eV (Fig. 2c, right), respectively. The Sb3d spin-doublet peaks have the energies 532.3 ± 0.2 eV and 541.7 ± 0.2 eV.

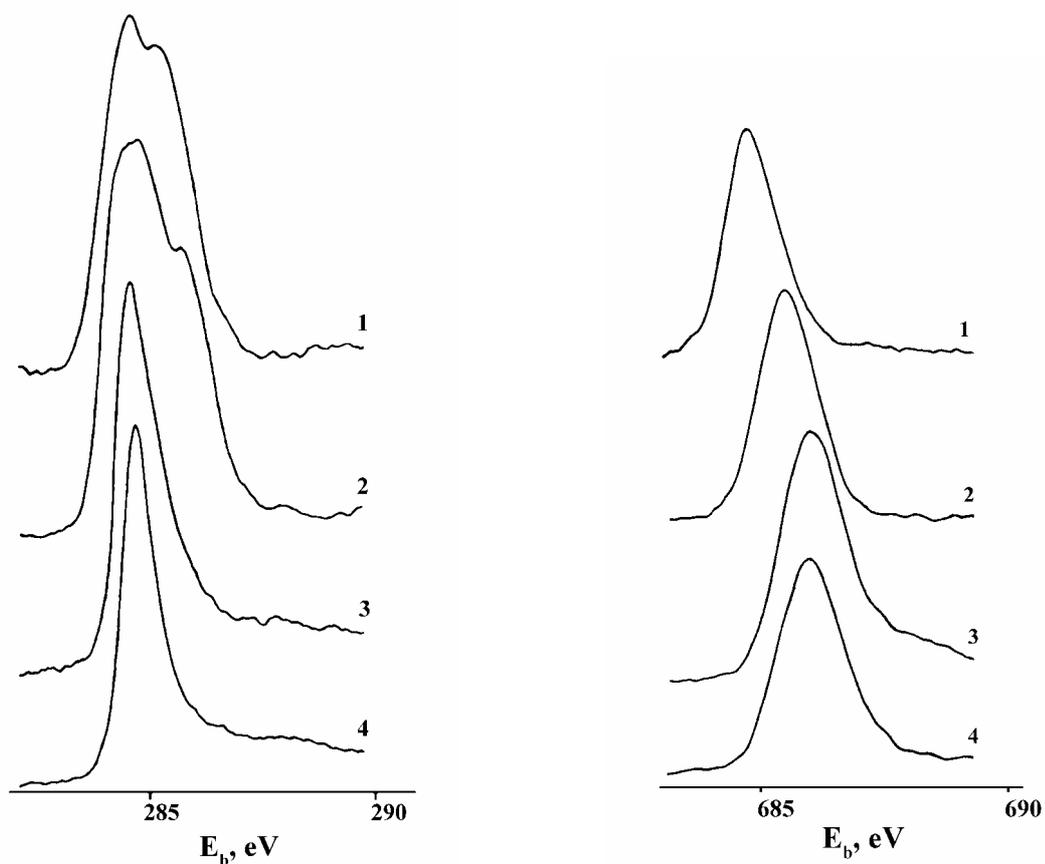


Fig. 2. The XPS C1s (left) and F1s (right) spectra of the $C_{22}NbF_5$ (1), $C_{13}TaF_5$ (2), C_xSbF_5 (3), C_8MoF_5 (4).

Table I. The ratio of carbon to oxygen (C/O) in GO samples investigated

No. (sample)	1	3	4	5	6	7	8	9	10	11	13
C/O	10.2	10.3	10.3	10.0	5.2	4.8	3.4	2.7	2.3	1.5	1.5

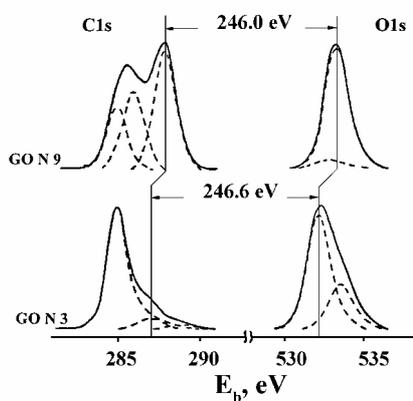


Fig. 3. The examples of C1s and O1s spectra of graphite oxides.

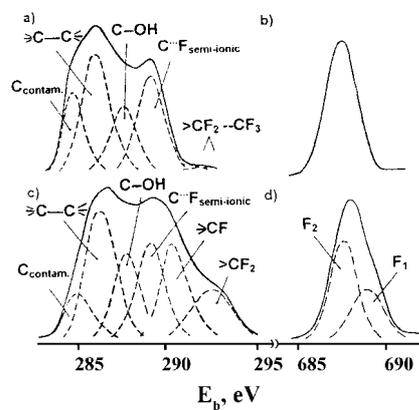


Fig. 4. The XPS C1s ('a' and 'c') and F1s ('b' and 'd') spectra of the fluorinated graphite oxide (FGO No. 8) and the fluorinated lignin (FL).

C_8MoF_5 . The C1s spectrum consists of single peak with the binding energy $E_b=284.3\pm 0.1$ eV (Fig. 2d, left). The F1s spectrum consists of a single peak with the binding energy $E_b=686.0\pm 0.1$ eV (Fig.3d, right). The Mo3d spin-doublet peaks have the energies 233.4 ± 0.1 eV and 236.1 ± 0.1 eV.

The differences in the F1s binding energies in C_xMeF_5 may be explained by different interaction of fluorine with the graphite matrix in the samples investigated.

We believe that the additional peaks in the C1s spectra of $C_{22}NbF_5$ and $C_{13}TaF_5$ compounds may be caused of partial surface degradation of the materials in consequence of contact with atmosphere water. No any lines corresponding to carbon-fluorine covalent bond and the MeF_3 molecules were registered in the samples investigated.

The X-ray photoelectron spectra of $C_{22}NbF_5$ are in good agreement with the spectra of C_8NbF_5 sample which were reported in Ref. [16]. But the synthesis conditions for C_8NbF_5 were differ than in our case. In the paper mentioned the NbF_5 intercalated into graphite with participation of elemental fluorine which oxidized carbon matrix. This way of synthesis allows the penetration of intercalate in the forms of NbF_6^- and polyions $(NbF_5)_nF^-$.

The results of our investigations show that oxidizing ability of NbF_5 , TaF_5 , SbF_5 , MoF_5 are sufficient for realization of mechanism of intercalation with partial transfer of the charge from graphene layers to the intercalate and formation of $C_x^{\delta+}MeF_5^{\delta-}$.

In the Figs. 2 the C1s and F1s XPS spectra of GIC C_xSbF_5 are presented. In the Sb3d spectrum a peak corresponding to SbF_3 also absents. In Ref. [11] the results of XPS investigation of C_xSbF_5 were reported. The F1s electrons gave two peaks corresponding to SbF_5 and SbF_6^- . In our case F1s electrons give the single broad line with $E_b=686.3\pm 0.1$ eV. Wortmann G. *et al.* [2] reported that the composition of intercalated layers in GIC with SbF_5 depends essentially on synthesis conditions and in some cases it may be present as polymerized macromolecules with common negative charge.

The results of C_xSbF_5 XPS spectra analysis may be also used for analysis of XPS data of GICs with Nb, Ta, Mo pentafluorides. For this compounds it means that 1) the binding energies of F1s electrons of MeF_5 and MeF_6^- are the same, as proposed for C_8NbF_5 [16], or 2) the intercalate layers consist of polymerized macromolecules $(nMeF_5^{\delta-})^-$.

FGO and FL. To investigate the influence of the modification of electron structure of the starting carbon materials on the results of next fluorination we had measured the XPS spectra of GO samples. The XPS spectra of some GO samples which were the starting materials for FGO synthesis are present in the Fig. 3

The main components of the C1s spectra of GO (Fig.3) with $N \leq 6$ have asymmetric line typical of conductive materials. This means that carbon atoms of the matrix keep sp^2 -hybridization. For the surfaces of the GO samples with $N > 6$, the matrix spectra lines become symmetrical (Fig.3). This means that on the surfaces of the samples hybridization of the matrix valent orbitals changes from sp^2 to sp^3 .

C1s spectra of the FGO samples of both phases measured consist of some basic lines (Fig. 4). Carbon line marked "semi-ionic" appears after interaction of GO samples with BrF_3 in all compounds under study. Consequently, this peak may be attributed to the carbon bound to fluorine. Fluorine peaks with binding energies equal 687.6 ± 0.5 eV were observed in the FGO spectra (Fig.

4b). This value of fluorine E_b is less than usually observed in covalent materials (689.6 ± 0.5 eV) both for aliphatic and cyclic forms [17]. The values of the modified Auger parameter α' of the fluorine spectra in FGO are 1342.8 ± 0.2 eV and differ from those observed in LiF (1339.8 eV) [18] and covalent fluorine carbon compound $-(CF_2-CF_2)_n-$ (1341.2 ± 0.2 eV). C1s peaks in the FGOs (Fig. 4a) with $E_b=289.3\pm 0.3$ eV may be attributed to semi-ionic carbon fluorine bonds. The data reported show that all used initial substances for FGO synthesis include fragments with unsaturated C-C bonds. XPS investigation of FL showed the presence of carbon peaks in the C1s spectrum (Fig.4c) which may be attributed to semi-ionic C-F bond (289.2 ± 0.2 eV), $\equiv CF$ (290.5 ± 0.2 eV) and $>CF_2$ (292.5 ± 0.2 eV). F1s spectrum of FL (Fig.4d) consists of two peaks with $E_b=687.8\pm 0.2$ eV (F_2) and $E_b=689.2\pm 0.2$ eV (F_1). Peak F_1 we attribute to the covalent C-F bonds and F_2 to the semi-ionic ones in accordance with their binding energies. Initial hydrolysed lignin also contains benzene aromatic with unsaturated C-C bonds. XPS data on FL show that the layered structure of initial substances is not necessary for the formation of semi-ionic bonds between fluorine and carbon.

4. CONCLUSION

We have studied by XPS method the fluorinated graphite oxides, graphite intercalation compounds (GICs) with NbF_5 , MoF_5 , TaF_5 , SbF_5 and fluorinated lignin.

In F1s spectra of fluorinated graphite oxides and fluorinated lignin was found a peak with the value of binding energies being intermediate between values in a typical ionic compound LiF and covalent compounds of type $(CF)_n$ and $-(CF_2-CF_2)_n-$. The substances under study, even at high oxidizer content at all synthesis stages contain structure fragments with carbon having sp^2 -hybridized orbitals of the valent electrons. The bond formed between fluorine and these fragments is of semi-ionic type at the used method of fluorination. The observation of semi-ionic state of fluorine in the FL allows to assume that the lamellar structure of initial substance is not necessary for the formation of semi-ionic bond between fluorine and carbon.

In all pentafluoride GICs the F1s spectra consist of a single peak.. In GICs with NbF_5 and TaF_5 the C1s spectra consist of two peaks. In the 3d spectra of Nb, Sb, Mo and 4f spectrum of Ta the peak corresponding to MeF_3 molecules was not observed. Basing on the XPS data the model of electronic structure was proposed for compounds investigated.

ACKNOWLEDGMENTS

The authors are thankful to Drs. A.K. Tsvetnikov, T.Yu. Nazarenko and L.A. Matveenko for the synthesis of the samples investigated. This work was supported by the grant from the Russian Foundation for Basic Research (No. 00-03-32610) and the grant from Russian Academy of Sciences for young scientists

References

- [1] Moran MJ, Fischer JE, Sal neck WR. Fractional ionization and the identification of intercalated species in AsF_5 -graphite. J. Chem. Phys. 1980; 73(2):629-636.

- [2] Workman G, Gilder F, Perched B, Kindle G, Scholl R. Chemical and micro structural organization of graphite intercalated with SbCl_5 and SbF_5 from ^{121}Sb -Mössbauer spectroscopy. *Synth. Met.* 1988; 26(2):109-137.
- [3] Watanabe N, Nakajima T, Touhara T. *Graphite Fluoride*. Amsterdam: Elsevier. 1988:87-89.
- [4] Nazarov AS, Makotchenko VG, Lisitsa VV. Low temperature graphite fluorides, graphite oxyfluorides, graphite "aminofluorides" and "amino-oxides". *Mat. Sci. Forum (ISIC-6)* 1992; 91-92: 10.
- [5] Panich AM. C-F Bonding in Fluorine-Graphite Intercalation Compounds and Graphite Fluorides: ^{13}C and ^{19}F NMR Study. *Bulletin of Magnetic Resonance* 1999; 20(1-4):20-24.
- [6] Hamwi A. Fluorine reactivity with graphite and fullerenes. Fluoride derivatives and some practical electrochemical applications. *Phys. Chem. Solids* 1996; 6-8:667-688.
- [7] Tressaud A, Moguet F, Flandrois S, Chambon M, Guimon C, Nanse G, Papirer E, Gupta V, Banl OP. On the nature of C-F bonds in various fluorinated materials: XPS and TEM investigations. *J. Phys. Chem. Solids* 1996; 57(6-8):745-752.
- [8] Koh M, Yumoto H, Higashi H, Nakajima T. Fluorine intercalation in carbon alloy C_xN . *J. Fluor. Chem.* 1999; 97:239-246.
- [9] Tsvetnikov AK, Nazarenko TYu, L.A.Matveenko LA, Nikolenko YuM. Peculiarities of BrF_3 intercalation into oxidized graphite. *Mat. Sci. Forum (ISIC-6)*1992; 91-92:201-208.
- [10] Salaneck WR, Brucker CF, Fischer JE, Metrot A. X-ray photoelectron spectroscopy of graphite intercalated with H_2SO_4 . *Phys. Rev.* 1981; B24(9): 5037-5046.
- [11] Joyner RW, Vogel FL. X-ray photoelectron spectroscopy studies of SbF_5 intercalated graphite. *Synth. Met.* 1981; 4(2):85-90.
- [12] Shcofield JH. Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. *J. Electron Spectrosc. Related. Phenom.* 1976; 8(2):129-137.
- [13] Yudin DV, Zelenskiy YuV. The possibilities of the dialog during spectrometric data treatment. *Zhurnal prikladnoy spektroskopii (Russia)* 1990; 52(3):445-451.
- [14] Zelenskiy YuV, Yudin DV. The previous treatment of the X-ray photoelectron spectra. *Zhurnal prikladnoy spektroskopii (Russia)* 1991; 54(1):40-45.
- [15] Nakayama Y, Soeda F, Ishitani A. XPS study of the carbon fiber matrix interface. *Carbon* 1990; 28(1):21-26.
- [16] Nakajima T, Okahara K, Padma DK, Watanabe N. Preparation and electrical-conductivity of niobium fluoride graphite-intercalation compounds. *Carbon* 1988; 26(6):825-829.
- [17] Nefedov VI. X-ray Photoelectron spectroscopy of Chemical Compounds. Moscow: Khimia (Chemistry), 1984:136-139.
- [18] Muilenberg GE *et al.* editors. *Handbook of X-ray photoelectron spectroscopy*. USA: Perkin-Elmer Corp., 1978: 43-45.