CHEMICAL AND SEM ELECTRON MICROSCOPY ANALYSIS FOR THE PYROLYTIC GRAPHITE FILM LAYED WITH ELECTRICAL DISCHARGES IN PULSE – EDI - PROCEDURE

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1. INTRODUCTION

Thermogravimetric analysis at which the pyrolytic graphite layed with EDI procedure was subjected, revealed a number of interesting observations such as mass additions at various temperature ranges. These interesting phenomena have led to further analysis at which the pyrolytic graphite layed with EDI procedure was subjected. The investigation consisted in a set of SEM electron microscopy analysis. This analysis aims to identify if besides the pyrolytic graphite film, after applying electrical discharges in pulse EDI treatment, is also obtain other chemical species responsible for the addition of mass such as fullerenes or carbon nanotubes which are spatial structures composed of carbon atoms sp^2 hybridized – C_{20} – C_{90} that are able to encapsulate inside their large molecule other small molecules N_2 , HOH [1, 2, 4].

In order not to induce errors in determinings, was avoided the using iron samples. Thus, to obtain samples was used silicon plate a non-magnetic material, chemically inert, which does not induce changes in the graphite film structure. The silicon has also good thermal shock resistance which are generated by the electrical discharges in pulse EDI.

2. ELECTRON MICROSCOPY SEM ANALYSIS OF THE SAMPLES

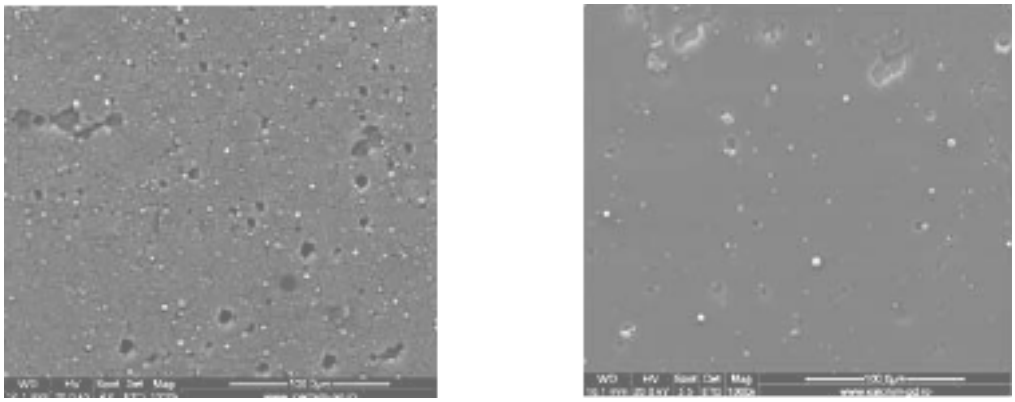
The silicon samples were submitted on an electron microscopy analysis type Quanta FEI Phillips a set of images have been obtained with magnification in the range (1000x – 20 000 x) for a large number of samples (Fig. 1).

From these images is clearly evidenced, that besides graphite film, was also obtained a series of globular formations with spherical shape, especially in images obtained for 2_001, 2_007 and 1_007 samples (Fig. 2 - 5). These spherical formations appear randomly on the sample surface and they due to the electrical discharges in pulse – EDI treatment. It is very clear that these formations it can not have another composition than carbon. It is

Figure 1. Electronic microscope Quanta FEI Phillips.

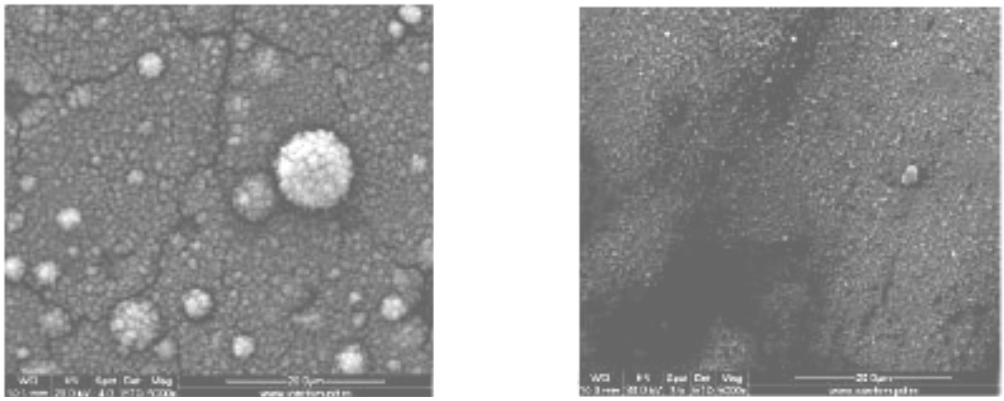
excludes that the these chemical species are produced by oxidation because the product of oxidation is gaseous CO_2 and it is eliminated from the system.

The resulting shape and the dimensions of these formations, from the images taken by electron microscopy, they are comparable to those of fullerenes, molecules spatial type with C 60 – C 80 [2]. These images bring a new argument in favor of a priori assertions regarding the occurrence of these chemical species - fulerene type - to application of the procedure of electrical discharges pulsed EDI.



a) b)

Figure 2. Sample 1_001, 2_001 magnification 1000x.



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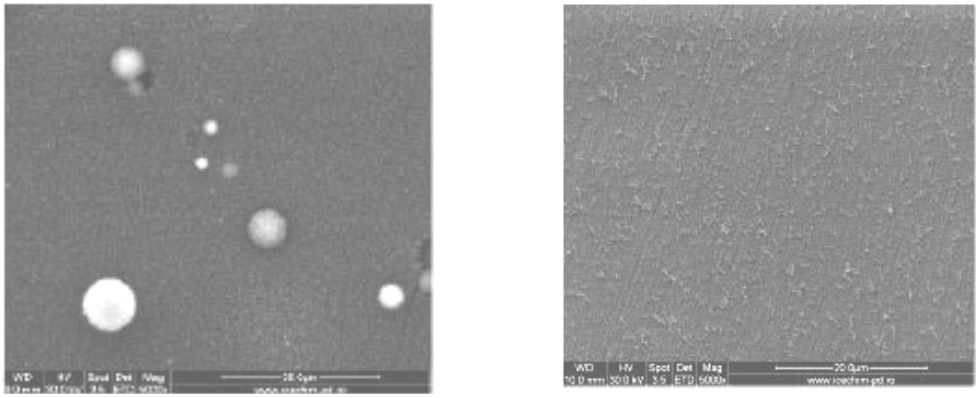
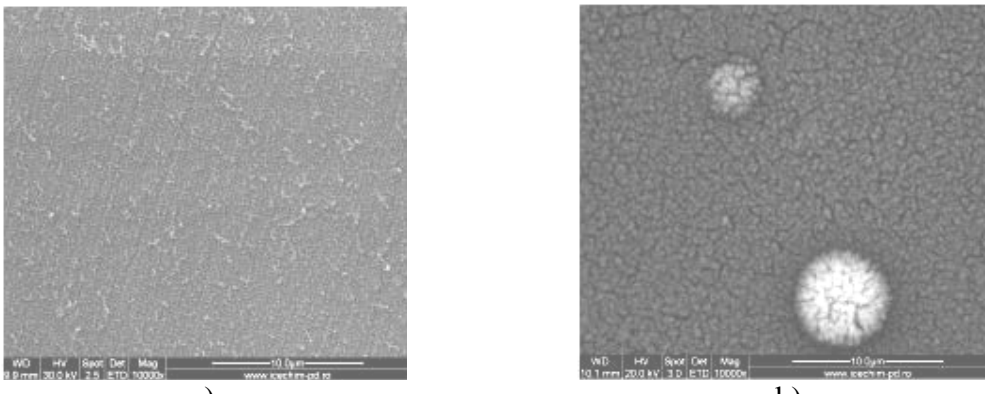


c) d)

Figure 3. Sample 2_001, 2_007, 1_007, 2_009 magnification 5000x



a) b)

Figure 4. Sample 2_009, 2_001 magnification 10 000x.

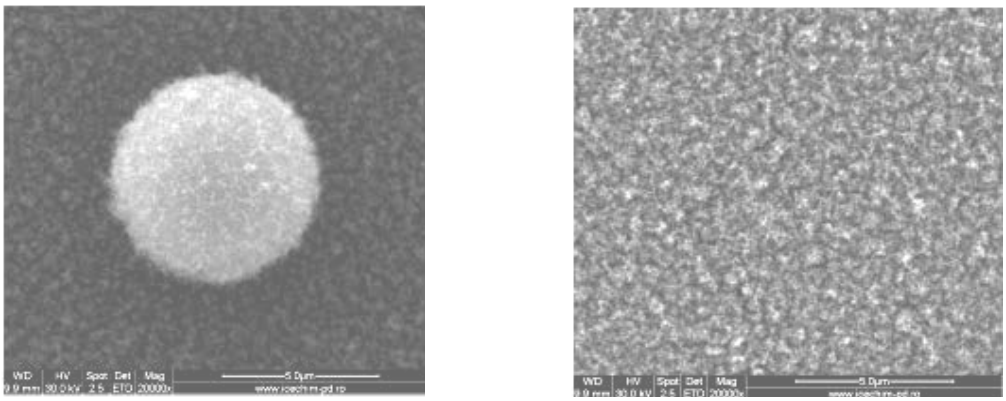


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Figure 5. Sample 2_007, 2_009 magnification 20 000x.

3. CHEMICAL ANALYSIS OF GRAPHITE FILMS OBTAINED BY THE PROCEDURE OF ELECTRICAL DISCHARGES PULSED EDI

Globular formations present on the surface of graphite film, obtained by the procedure of electrical discharges in pulsed EDI, and the mass addition phenomenon observed, have led to the preliminary conclusion that besides graphite film itself mostly, of which is composed the deposited film on the metallic surface of the target, was also obtained a number of other carbon chemical species [3, 4]. Starting from the idea that these globular formations are compounds of carbon, with spatial molecules fullerenes and / or nanotubes type, with relatively high number of carbon atoms, (60 – 80), the samples 1_007 – 2_009, previously subjected to a non-destructive SEM microscopy analysis, have been subjected subsequently to chemical analysis. The chemical analysis of samples, consisted of their treatment with many organic solvents [5], for 48 hours, under continuous stirring (tab. 1). The best results were obtained in case of using α-chloronaphthalene, in which the carbon spatial formations have the highest solubility. Samples were conditioned for 48 hours by maintaining them in a dry atmosphere, for bringing them to constant mass. The sample was maintained in a dessicator until two successive weighings performed at an interval of 6 hours lead at the same value.

The sample 2_001, where the phenomenon of globular formations appearance is most significantly, was subjected to the action of organic solvents. The most semnificative results were obtained in case of using α-chloronaphthalene. The sample was maintained in α-chloronaphthalene for

Tab. 1. The solubility of spatial C60 in various organic solvents.

The solubility of spatial C60 in various organic solvents (S, mg/mL)	
Solvent	**S**
1-chloronaphthalene	51
1-methylnaphthalene	33
1,2-dichlorobenzene	24
1,2,4-trimethylbenzene	18
tetrahydronaphthalene	16
carbon disulfide	8
1,2,3-tribromopropane	8
xylene	5
bromoform	5
cumene	4
toluene	3
benzene	1.5
carbon tetrachloride	0.447
chloroform	0.25
n-hexane	0.046
cyclohexane	0.035
tetrahydrofuran	0.006
acetonitrile	0.004
methanol	0.00004
water	1.3×10^{-11}
pentane	0.004
octane	0.025
isooctane	0.026
decane	0.070
dodecane	0.091
tetradecane	0.126
dioxane	0.0041
mesitylene	0.997
dichloromethane	0.254

48 hours under continuous stirring. At every 6 hours the samples - silicon plates coated with graphite film - they were extracted from the environment of α-chloronaphthalene using tweezers and subsequently maintained in a dessicator for one hour for complete drying. After the drying of the sample it has weighed on a microbalance. The procedure of maintaining in solvent, extraction, drying and weighing it was undertaken at every 6 hours for 48 hours. As the result of the set of successive weighings it is found for the sample coded 2_001 a significant mass loss. The schedule for the mass loss, corresponding the sample coded 2_001 it is presented in tab.3.2 and in figure 6

Figure 6. Sample 2_001 in α-chloro-naphthalene under continuous stirring.

Table 2. The schedule for the mass loss, corresponding the sample coded 2_001 for 48 hours

Sample code	**Initial mass ,g**	Measurement interval, hours,							
		6	12	18	24	30	36	42	48
	ά Cl naftalina								
2_001	**5.7998**	5.7997	5.7997	5.7996	5.7996	5.7995	5.7995	5.7995	5.7994

As a result of the action of α-chloronaphthalene, the coded sample 2_001 suffers a significant loss of mass – 0.4 mg - perceptible for measuring instruments (from 5.7998g to 5.7994g). This fact indicates that some component of graphite film it is removed by solubilisation as shown in Table 2 and figure 7.

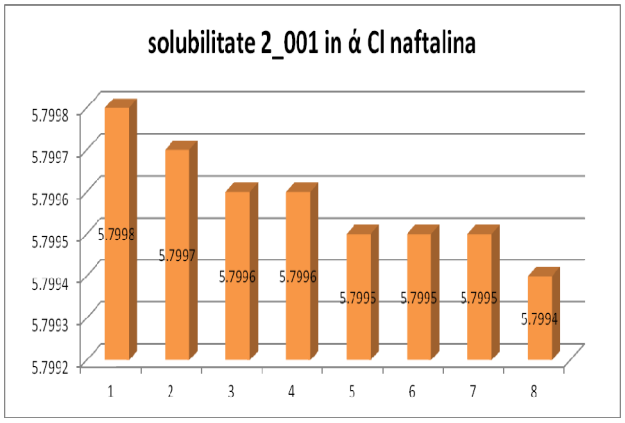
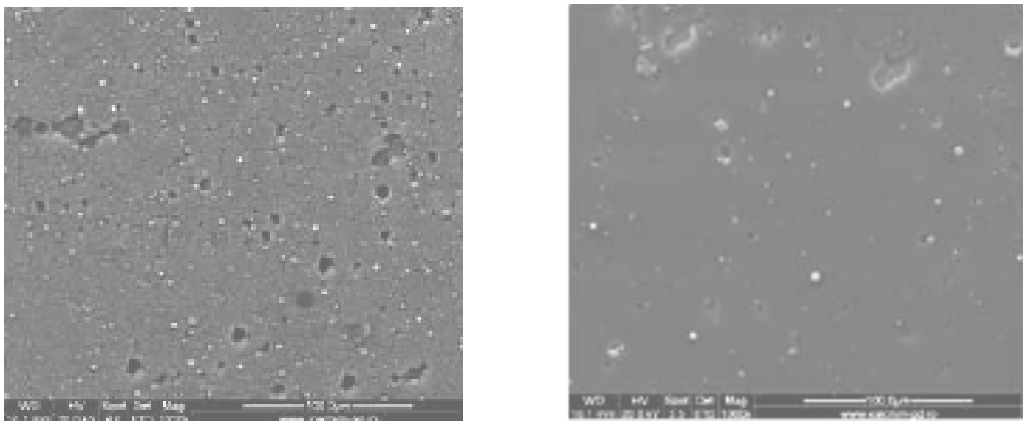


Figure 7. The schedule for the mass loss, corresponding the sample coded 2_001 for 48 hours

4. ELECTRON MICROSCOPY SEM ANALYSIS OF GRAPHITE FILMS 2_001 SAMPLE OBTAINED BY THE PROCEDURE OF ELECTRICAL DISCHARGES PULSED (EDI) AFTER THEIR MAINTAINING IN ENVIRONMENT OF A-CHLORONAPHTHALENE

The coded 2_001 sample, which is the most representative sample, after the action of α-chloronaphthalene for 48 hours, it was subject to a new electron microscopy SEM analyse. Following this further analysis in electron microscopy SEM it has been found that a large part of globular formations have been removed. In fig. 8 they are shown the initial SEM image (above) and the final image (below) after the action of α-chloronaphthalene for 48 hours.

Consulting comparatively SEM images taken before and after the action of α-chloronaphthalene for 48 hours major differences have been found between the initial stage and final stage of the graphite film deposited by the procedure of electrical discharges in pulsed EDI. Thus, before the action of α-chloronaphthalene for 48 hours the presence of these globular formations is more pronounced. After the action of α-chloronaphthalene for 48 hours the presence of these globular formations have been substantially reduced. The conclusion is that the mass difference of 0.4 mg, is due to the dissolution of these formations in α-chloronaphthalene.



a) b)

Figure 8. Sample 2_001 before and after the action of α-chloronaphthalene for 48 hours.

CONCLUSIONS

This paper presents the research activities who aimed to analyze the graphite film obtained by the procedure of electrical discharges in pulse EDI with a cathode made of pyrolytic graphite. Graphite film deposited on the surface of silicon plates have been subjected to an electron microscopy SEM analyse. As a result of this analyse, a number of spherical formations were observed on the surface of the graphite film. Subsequent to the SEM analyse, the samples were submitted to the action of α-chloronaphthalene for 48 hours. After the action of α-chloronaphthalene it was found that most of these formations have been removed due to the dissolution of these formations in α-chloronaphthalene. The sample 2_001, is most significantly. Here the phenomenon of globular formations appearance it was most visible. Following these sets of analyzes a series of interesting scientific information have been achieved. Thus after the procedure of electrical discharges in pulsed EDI, outside of the graphite film have also obtained a number of spatial formation of carbon atoms sp2 hybridized fullerenes and / or carbon nanotubes

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