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RAMAN SPECTRA ANALYSIS OF CARBON LAYERS ON MAGNESIUM ALLOYS

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Abstract - In this paper we deal with the investigation of the thin diamond-like layers (DLC) manufactured on magnesium alloys (AZ31) using Plasma Activated Chemical Vapour Deposition (PACVD) method. Raman spectroscopy investigation has been carried out for determining both layer composition and fraction of the diamond-like structure in the layers. The Raman spectroscopy is recognized as the main tool used for surveying of the allotropic content of the carbon layers. It is imposed by the necessity of the distinction not among the different chemical elements but among different bonds of the same chemical element-carbon, or alternatively-among different bonds of carbon with a few other chemical elements-especially hydrogen. During the Raman spectra analysis, both qualitative and quantitative analysis are performed, which is essential for the use of the carbon coatings in the broad range of mechanical technologies. A tool used in these investigations is Voigt peak profile based on Faddeeva function, allowing a very precise comparison of spectra with elimination of specificity of measurement equipment.

Résumé - Elaboration et Analyse Raman de Dépôts Carbone sur des Alliages de Magnésium. Ce travail présente l'étude de revêtements diamant-similaire couches (DLC) sur des alliages de magnésium (AZ31), élaborés à l'aide du procédé CVD assité plasma (PACVD). Afin d'analyser leur structure et de donner une composition quantitative, de la spectroscopie Raman a été utilisée. Il est couramment admis que la spectroscopie Raman est l'outil le mieux adapté pour étudier la composition allotropique des couches diamant. Il est nécessaire de connaître la nature des liaisons entre les différents atomes de carbone ou entre le carbone et d'autres éléments, notamment l'hydrogène. L'étude poussée de spectres Raman permet de donner des informations non seulement qualitatives mais également quantitatives sur la structure des revêtements diamant, ce qui est essentiel en vue de leurs larges domaines d'applications potentiels. Dans cette étude, le profil de Voigt basé sur la fonction Faddeeva a permis de comparer différents spectres tout en s'affranchissant des spécificités des instruments de mesure.

1. INTRODUCTION

Magnesium alloys belongs to the lightest structural engineering materials, and therefore, particularly attractive for structural usage where weight reduction is of significant concern [9]. In this paper we studied the thin diamond-like layers (DLC) manufactured on AZ31 magnesium alloys using Plasma Activated Chemical Vapour Deposition method (PACVD). These layers have been investigated thoroughly using different methods [6,9]. A few of this methods has been of mechanical

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type, related with mechanical properties of the coatings: nanoindentation and profile cut for measurement of the layer thickness [6], and scratching and friction tests for measurement usability merit of the layer. Also Raman spectroscopy investigation has been carried out for determining both layer composition and fraction of the diamond-like structure in the layers. Examination of the layers imposing procedure shows [5], that different carbon allotropes could be expected in the layer, not only diamond-like. Although efforts have been made to enhance the content of the diamond-like structures, it is not possible to obtain a pure one.

2. MANUFACTURING OF CARBON LAYERS

The carbon layers on the AZ31 magnesium alloy samples have been fabricated with using PACVD method, in the device presented in *figure 1* [6-8]. This method relays mainly on decomposition of a hydrocarbon (methane) in the electromagnetic field of the high frequency 13.56 MHz, conducted in the processing chamber environment at the pressure in the range of 10-20 Pa, and temperature of about 150˚C (423 K). The selection of this method has been made up taking into account its wide availability, low costs of the layer fabrication as well as the very good technological results of layers used in different purposes: on steel substrate for medical purposes, as colored coatings in the jewellery, and for machine industry as coatings of the cutting tools.

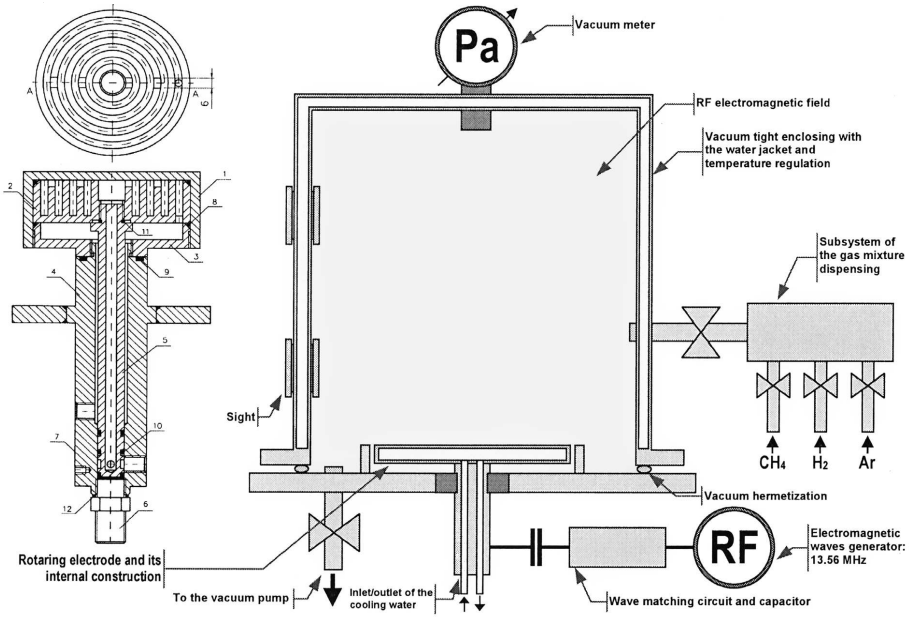

Figure 1. The schematic diagram of the device for the PACVD method carbon coatings synthesis. Electrode construction details: 1 – outer case, 2 – cooling spacer, 3 – cap, 4 – outer spindle, 5 – inner spindle, 6 – pressing screw, 7 – washer, 8-12 – tightening rings

3. RAMAN SPECTROSCOPY OF CARBON LAYERS

Investigations have been carried out using Advanced Research Raman System Yobin-Yvon T-64000. The raw spectra from the laser Raman spectrometer for five different samples of the carbon layer on the AZ31 magnesium alloy are shown in *figure 2*. The preliminary analysis of the

experimental Raman spectra indicates the necessity of some standardization i.e. bringing the spectra to the same base line. It demands a model of the whole measurement of which final result establish one of the curves from the *figure 2* [5,8].

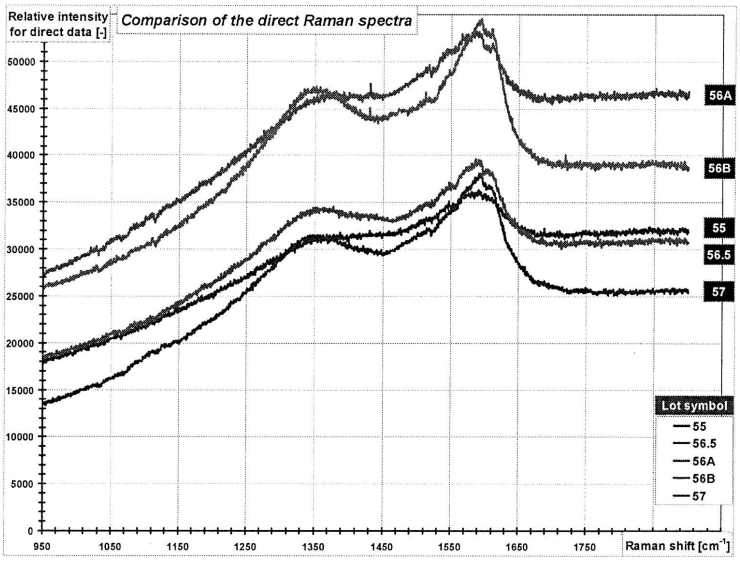

Figure 2. The raw spectra from the laser Raman spectrometer for five different samples of the carbon layer manufactured on the AZ31 Mg alloy; laser type Ar 514,5 nm, laser power 50 mW

4. RAMAN SPECTRUM DESCRIPTION

One act of resonance radiation absorption and emission during generation of the Raman scattering could be described with widely known Breit-Wigner-Fano curve, especially in lower part of Raman spectrum, related with disordered carbon [3,5]:

$$I(k) = \frac{I_0}{1 + S \cdot (k_0 - k)^2} \tag{1}$$

where:
I_0 - maximal relative intensity of the peak, [-],
S - parameter of the peak width (greater when peak is narrower), [cm^2],
k_0 - wave vector for the maximal intensity of the peak, [cm^{-1}].

For our investigations this model is not appropriate because we looked for model valid for the all types of carbon structures one can meet in carbon layers made with PVD process. Then we have evaluated Raman spectrum of the layer using Gaussian peaks and exponential baseline function. We have applied the following model curve of intensity I versus wave number k:

$$I_G(k) = \sum_{n=1}^{N} I_{0_n} \cdot \exp\left[-S_n \cdot \left(k - k_{0_n}\right)^2\right] + \left(I_{B_{MAX}} - I_{B_{MIN}}\right) \cdot \left(1 - \exp(-S_B \cdot k\right) + I_{B_{MIN}} \tag{2}$$

where:
I_{0n} - maximal relative intensity of the n-th peak, [-]
S_n - parameter of the n-th peak width (greater when peak is narrower), [cm^2],
k_{0n} - wave vector for the maximal intensity of the n-th peak, [cm^{-1}],
I_{Bmax} - maximal relative value of the baseline function,

I_{Bmin} - minimal relative value of the baseline function,
S_B - parameter of the baseline function growth, [cm].

One of the benefits of the above model is its computational simplicity. None of the function used demands special evaluation, like in the case of Voigt profile mentioned later.

Least squares (RMS) approximation has been used for determination of the parameters in the model (2). The residual error behavior has been investigated to establish "end of model complication" i.e. number of carbon structures taken into account. The set of expected carbon structures is listed in *table I.* Initial data related with peaks allocation for given carbon forms have been gathered from a number of different publications. In a case of controversy averaged data has been admitted. Global results of model fitting are collected together and exhibited in *figure 3* [5].

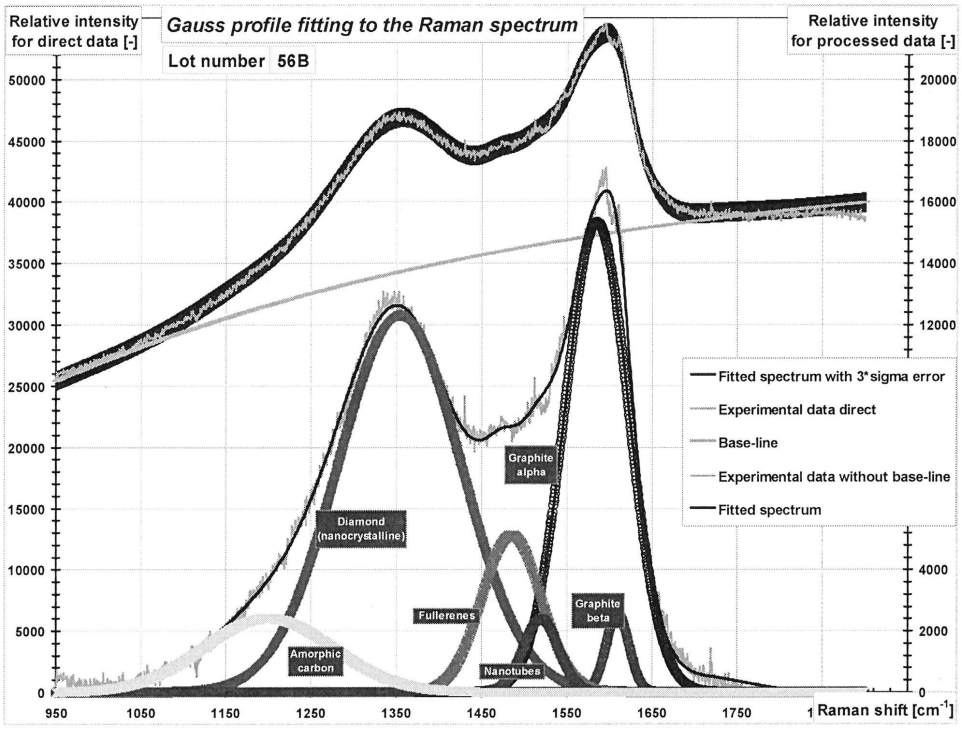

Figure 3. Exemplary results of Raman spectrum evaluation using Gaussian profile (2)

Table I. Results of the carbon structures' yield estimated with profile (2)

Gaussian profile fitting results				
Investigated structure	Peaks			Yield
	Location	Height	Width	
	[cm^{-1}]	-	[cm^{-1}]	%
Amorphic carbon	1200.00	2414.29	75.67	9.10
Diamond (nanocrystalline)	1354.00	12311.58	72.12	45.41
Rings: antracenes, fenantrenes, etc.	1474.00	285.42	16.89	0.20
Fullerenes	1485.00	5125.65	34.55	9.26
Nanotubes	1520.00	2378.46	48.77	2.59
Graphite alpha	1585.00	15332.08	37.27	29.95
Graphite beta	1610.00	2552.56	13.44	1.80
Chains from hydrocarbons	1700.00	3687.81	60.73	1.70

Voigt profile given in the form (3) is a specific convolution function with two parameters, which cover both spectrum features origin from the investigated medium and influence of the Fabry-Perrot interferometer usually applied as the radiation sensor and filter [2,3]:

$$V(x,\sigma,\gamma)=\int_{-\infty}^{+\infty}G(t,\sigma)C(x-t,\gamma)dt \tag{3}$$

where:

$G(x,\sigma)$ - centered Gaussian distribution modeling the features of the investigated medium with one parameter σ describing natural peak width:

$$G(x,\sigma)=\frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{x^2}{2\sigma^2}} \tag{4}$$

$C(x,\gamma)$ - centered Cauchy (Lorentz) distribution modeling influence of the Fabry-Perrot interferometer, with one parameter γ describing width of spectral resolution:

$$C(x,\gamma)=\frac{\gamma}{\pi\left(x^2+\gamma^2\right)} \tag{5}$$

Voigt profile in the analytical form (after integration in the convolution) could be expressed as:

$$V(x,\sigma,\gamma)=\frac{\mathrm{Re}[F(z)]}{\sigma\sqrt{2\pi}} \tag{6}$$

where complex variable z is related with current variable x and parameters σ and γ as:

$$z=\frac{x+j\gamma}{\sigma\sqrt{2}} \tag{7}$$

where in turn $F(z)$ is a complex error function known also as Faddeeva function:

$$F(z)=e^{-z^2}\cdot erfc(-jz) \tag{8}$$

where in turn $erfc(z)$ is complementary error function expressed as:

$$erfc(z)=\frac{2}{\sqrt{\pi}}\int_x^{\infty}e^{-z^2}dz \tag{9}$$

Some difficulties which usually arise with efficient use of the Voigt profile are caused by need of efficient calculation of the function *erfc*, which is not an analytical function. A number of methods is known including recently developed [1,2], but in our investigations we have used very simple and reliable solution – Taylor series expansion which in this case converges on the whole z-plane because *erfc* function is holomorphic over the whole z-plane:

$$erfc(z)=1-erf(z)=1-\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n+1}}{n!(2n+1)} \tag{10}$$

For Voigt profile we have applied the following model curve of intensity I versus wave number k, very similar to the Gaussian model (2) – base-line approximation was exactly the same, which allowed better comparison between models:

$$I_V(k)=\sum_{n=1}^{N}I_{0_n}\cdot V(k-k_{0_n},\sigma_n,\gamma)+\left(I_{B_{MAX}}-I_{B_{MIN}}\right)\cdot\left(1-\exp(-S_B\cdot k)\right)+I_{B_{MIN}} \tag{11}$$

Meaning of variables and parameters is the same as for the model (2). Results of fitting are provided in *figure 4* and *table II* [5].

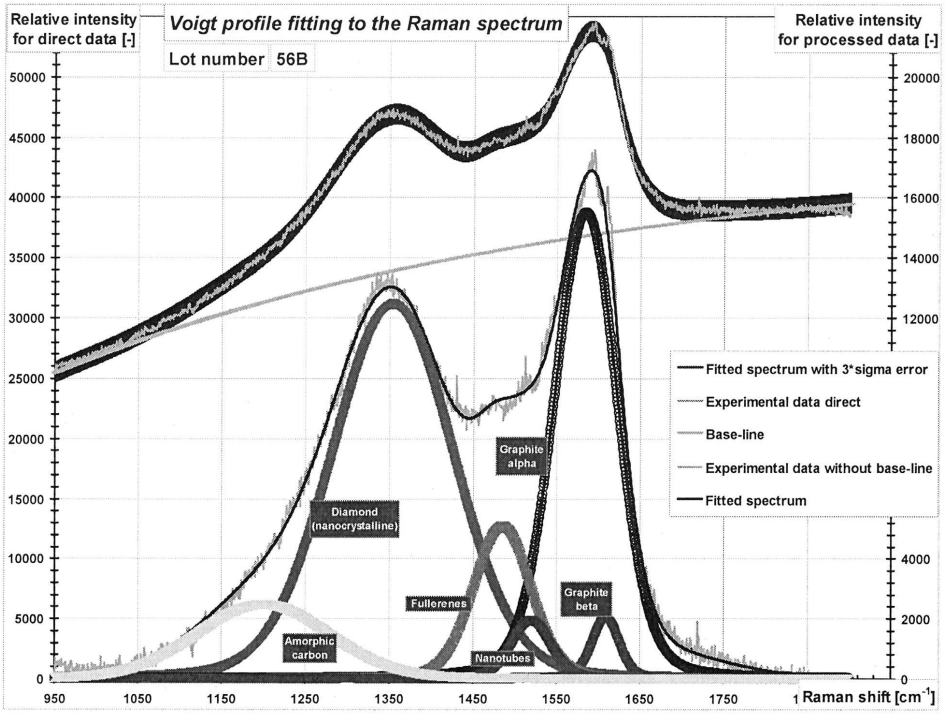

Figure 4. Examplary results of Raman spectrum evaluation with using Voigt profile (11)

Table II. Results of the carbon structures' yield estimated with profile (11)

Voigt profile fitting results					
Investigated structure	Peaks				Yield
	Location	Height	Width		
			Gauss	Cauchy	
	[cm^{-1}]	-	[cm^{-1}]	[cm^{-1}]	%
Amorphic carbon	1200.00	2662.22	75.79	7.11	9.34
Diamond (nanocrystalline)	1354.00	13754.90	68.45	8.64	44.81
Rings: antracenes, fenantrenes, etc.	1474.00	286.70	16.93	6.82	0.19
Fullerenes	1485.00	5966.53	31.25	6.48	9.10
Nanotubes	1520.00	2471.52	49.71	6.64	2.49
Graphite alpha	1585.00	18341.60	34.25	7.58	30.66
Graphite beta	1610.00	2718.51	13.83	5.37	1.85
Chains from hydrocarbons	1700.00	3718.25	60.98	7.36	1.56

5. RESULTS AND DISCUSSION

Results concerned total comparison of different carbon forms in carbon layers deposited on AZ31 magnesium alloys usig PACVD technology. Analysis of results obtained for individual specimens produced within the scope of the planned experiment (specimens 1÷5), revealed that the diamond phase and alfa-graphite phase have dominated in the deposited layers. Also other carbon phases have been identified, such as beta-graphite, fullerens, nanotubes and other, including some unidentified forms, but their contents are minor. In the *figure 5* the comparison of the total Raman spectra of these carbon layers are presented. Also in the *figures 6 - 8* the Raman spectrum decomposition is presented with main allotropic components of the carbon layer (nanocrystalline diamond, graphite α, graphite β, fullerens, nanotubes and amorphic carbon) for the five ultra-thin layers fabricated on the AZ31 magnesium alloy. All of the calculations have been performed in the

Excel spreadsheet with using the Solver tool with the following settings: searching with using of the Newton method, the automatic scaling at the every step, parabolic approximation of the error function shape (hipersurface) in the vicinity of the solution.

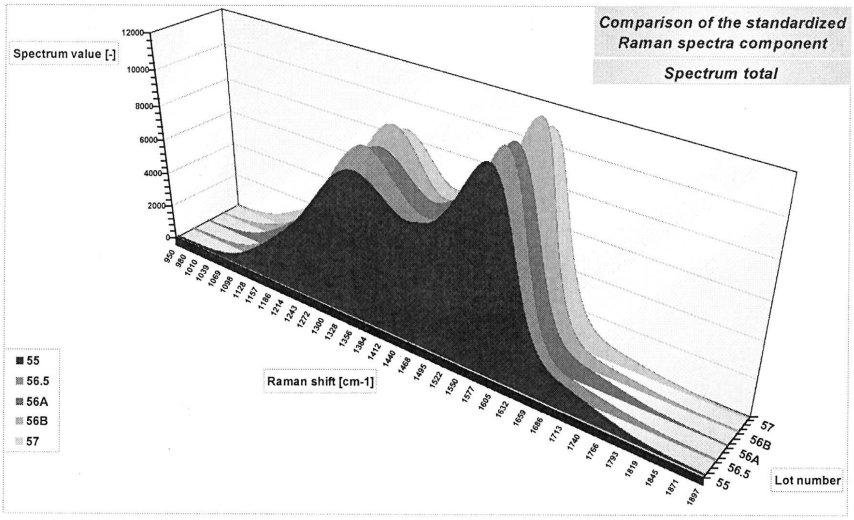

Figure 5. The comparison of the total, standardized Raman spectra of the carbon layers

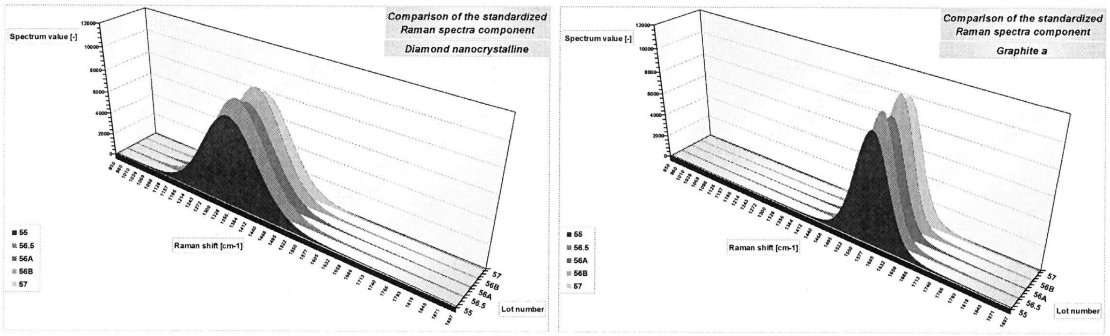

Figure 6. The comparison of the nanocrystalline diamond and α graphite component in the standardized Raman spectra of the carbon layers of the surveyed samples

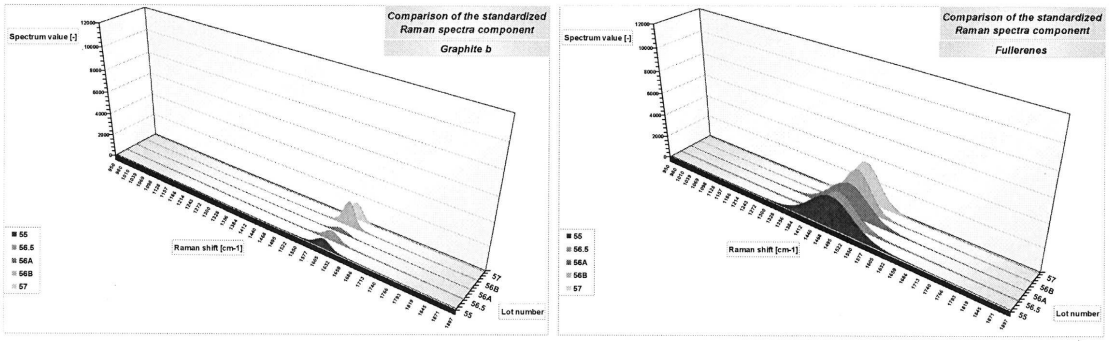

Figure 7. The comparison of the β graphite and different sizes fullerenes component in the standardized Raman spectra of the carbon layers of the surveyed samples

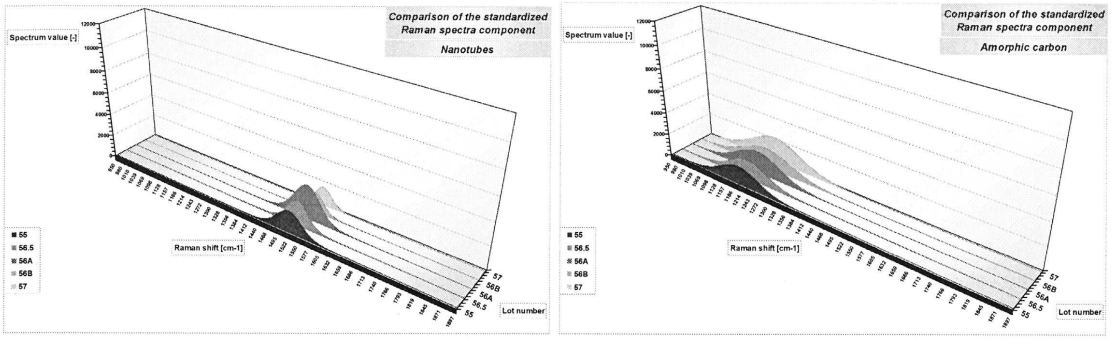

Figure 8. The comparison of the different sizes nanotubes and amorphic carbon component in the standardized Raman spectra of the carbon layers of the surveyed samples

6. CONCLUSIONS

The Raman method using the Voigt peak profile as the basic mathematical model, allowed to survey the allotropic content of the carbon coatings with the great reliability, precision and repeatability. This has the substantial cognitive meaning as well as the technological one – leading to the fabrication of coatings with defined parameters, working in the planned conditions. This is also the aim and purpose of the further exposed works related with the mathematical modeling of the carbon deposition on the metal alloy base.

It is possible to formulate the conclusion that when analyzing a carbon layer of known and reproducible structure it could be adequate to use Voigt profile for better precision of quantitative estimation of content of different carbon structures. When carbon layer technology is under development, it seems to be more adequate to use Gaussian profile for its better ability of determination of presence of different carbon structures even with loss of some precision in quantitative analysis.

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