METALLIC NANOPARTICLES AND NANOWIRES FROM VARIOUS AQUA SOLUTIONS

K. Alexandrova, I. Markova-Deneva, I. Dragieva

Abstract
Isotropic and anisotropic by shape nanomaterials (nanoparticles and nanowires) by chemical reduction method from various aqua solutions of salts and more specifically Ni nanoparticles from Ni salts with different anion content, as well as Ni nanowires using ceramic supports but without applying the "template" technique have been synthesized .The influence of the water complexes and their anion content on the formation mechanism of nanopartiles and nanowires has been investigated.
The supports with different chemical element contents and various specific surface areas (SSA) have been used to obtained nanowires. The influence of the wetting procedure of the support surface and the effect of the inserted support quantity as a weight ratio to Ni on the nanowire formation has been investigated.
Both nanostructure surface element content and binding energy of the electrons from different quantum levels have been determined by XPS.
Keywords: nanoparticles, nanowires, chemical reduction method, Ni salt solutions

INTRODUCTION

Recently a lot of data on obtaining isotropic and anisotropic by shape nanomaterials by chemical and electrochemical methods have been published [1-3]. Metal nanoparticles and nanowires by chemical method from aqua solutions of different salts have been synthesized [4-6]. Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and BET method investigations have been made [7-9].

Our work team has synthesized isotropic and anisotropic by shape Ni nanoparticles by the $NaBH_4$ chemical reduction method from various aqua solutions of Ni salts with different anion content, respectively Ni nanowires using different ceramic supports [10-13]. The aim of this work is to investigate the influence of the anion content of the water complexes on the formation of isotropic or anisotropic by shape nanosized materials and the creation of Ni-Ni or Ni-B, H chemical bonds, as well as the influence of the support with different chemical element content and various specific surface area on the formation of nanostructures. The influence of the wetting procedure of the support surface and the effect of inserted support quantity as a weight ratio to Ni on the specific surface area of nanoparticles and nanowires has been investigated. Their grain size, diameter, and weight percentage content of the included elementary nickel and boron and the precipitated support have been investigated as well.

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EXPERIMENTAL SECTION

Ni salts with a different anion content: $NiSO_4.6H_2O$, $NiCl_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and $NiBr_2.3H_2O$ and $NaBH_4$ water solutions identical in concentration and with equal volumes (0.086 M Ni salt solutions and 0.161 M $NaBH_4$ solutions) have been used.

The nanostructures have been synthesized in a reactor of ideal mixing where both Ni salt and $NaBH_4$ water solutions were mixed using a mechanical stirrer during the reduction process. The synthesis is carried out at room temperature, atmospheric pressure, in an open lab space without use of both protective gases and inert atmospheres.

Three different supports with various chemical nature (element content) and different SSA: SiO_2 (SSA=189. 5 m^2/g), SiMCM (SSA=349 m^2/g) and AlMCM (307 m^2/g) have been used for obtaining nanowires. The introduction of the support has been performed by two variants of wetting procedure of the support surface. The first one is named A-variant (the support is introduced with the Ni salt solution to the reducing agent solution) and the second one is named B-variant (the support is introduced with the reducing agent solution to the Ni salt solution).A metal/support weight ratio was from 10/0.3.

The nanomaterials morphology has been characterized by a scanning electron microscopy (SEM) with a microscope JEM 200CX-JEOL Japan, and a scanning appliance SID 3D. The specific surface area of the nanostructures and the supports used has been determined by the BET method (AREA meter, Strohlein in nitrogen flow at the temperature 78 K). Boron weight percentage content of the samples has been analytical determined by chemical method. Nickel and support weight percentage contents have been determined by a quantitative chemical analysis including the SEM microanalyser (Apparatus JEOL Superprobe-773 SEM/microanalyser and mounted System 5000 (HNU SYSTEM) EDS X-ray system with a Si (Li) detector).

The binding energy of the electrons and the element content on the nanostructures surface have been measured by X-ray photon spectroscopy (XPS) with an Escalab apparatus mark 2 - VG Scientific.

RESULTS SECTION

Influence of the Ni salts anion content on the formation of nanosized materials

Figures 1 to 4 present SEM micrographs of nanostructures (nanoparticles and nanowires) obtained from aqueous solutions of sulfate ($NiSO_4.6H_2O$), chloride ($NiCl_2.6H_2O$) and bromide ($NiBr_2.3H_2O$) complexes on SiO_2 support, as well as weight Ni/SiO_2 ratio = 1 and A-variant of the support wetting procedure.

The structure of the water ion complexes of sulfate ($NiSO_4.6H_2O$) has a major significance for obtaining anisotropic by shape nanostructures – Ni is deposited on SiO_2 support as nanowires with SSA = 59.25 m^2/g, while the structure of water ion complexes of chloride ($NiCl_2.6H_2O$) and bromide ($NiBr_2.3H_2O$) determines the obtaining of isotropic by shape nanomaterials – Ni is deposited as nanoparticles**,** respectively with SSA = 72.85 m^2/g and SSA = 55.14 m^2/g.

Figures 5 and 6 present SEM micrographs of nanowires obtained from water ion complexes of sulfate ($NiSO_4.6H_2O$) and nitrate ($Ni(NO_3)_2.6H_2O$) on SiO_2 support, as well as A-variant of support wetting procedure, but the weight Ni/ SiO_2 ratio = 0.66.

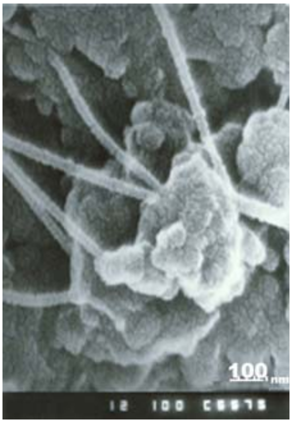

Fig.1. SEM micrograph of NiB/SiO_2 nanowires obtained from $NiSO_4$ SSA=59.23 m^2/g, Ni/SiO_2=1.

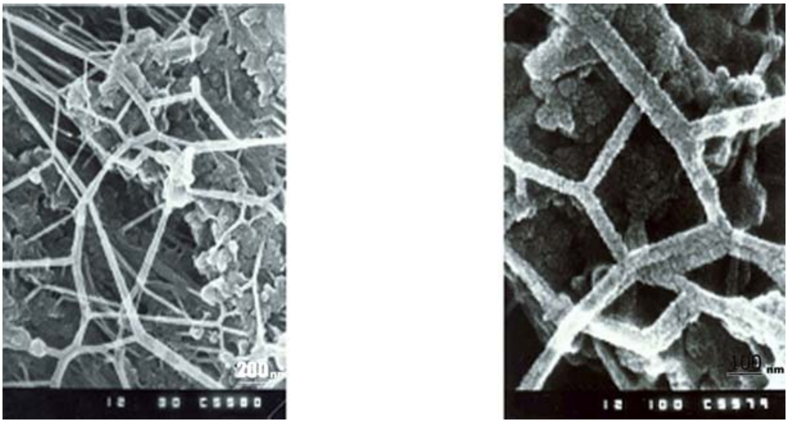

Fig.2. SEM micrograph of NiB/SiO_2 nanowires obtained from $NiSO_4$, SSA=59.23 m^2/g, Ni/SiO_2=1

Fig.3. SEM micrograph of NiB/ SiO_2 nanoparticles obtained from $NiCl_2$, SSA=72.85 m^2/g, Ni/SiO_2=1.

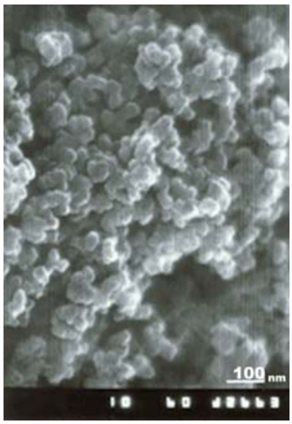

Fig.4. SEM micrograph of NiB/ SiO_2 nanoparticles obtained from $NiBr_2$, SSA=55.14 m^2/g, Ni/SiO_2=1.

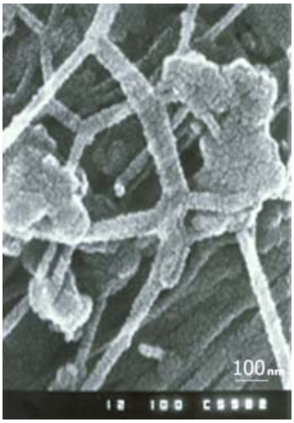

Fig.5. SEM micrograph of NiB/ SiO_2 nanowires obtained from $NiSO_4$, SSA=67.18 m^2/g, Ni/SiO_2 =0.66.

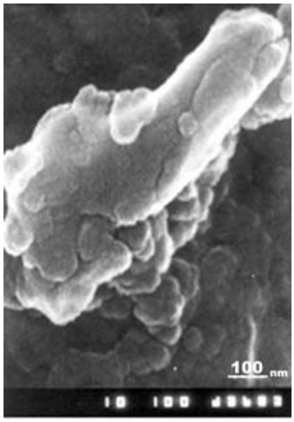

Fig.6. SEM micrograph of NiB/ SiO_2 nanowires obtained from $Ni(NO_3)_2$, SSA=96.34 m^2/g, Ni/SiO_2 =0.66.

In this case of sulfate and nitrate solutions a formation of nanowires is observed (with SSA = 67.18 m^2/g and SSA = 96.34 m^2/g respectively).

DISCUSSION

The anion content of the Ni salt solutions determines the formation of isotropic or anisotropic by shape nanostructures [4,5].

The two-element anions of the Ni complexes (SO_4, NO_3) determined nanowire formation, while in the case of single-element anions of the Ni complexes (Cl, Br) nanoparticles are formed.

In the case of $NaBH_4$ reduction in $NiCl_2$ or $NiBr_2$ water solutions with a mechanic stirring a three-dimensional nucleation of spherical nanoparticles - 3D mode of Volmer – Weber can be expected and a strong metal-metal (Ni-Ni) chemical bond can be created.

The metal-metal (Ni-Ni) bond strength will be greater than the metal-nonmetal bond strength:

$$\varphi_{Ni\text{-}Ni} > \varphi_{Ni\text{-}B,\, H}$$

In the case of two-element anions (a reduction in $NiSO_4.6H_2O$ and Ni $(NO_3)_2.6H_2O$ water solutions) the mechanism includes the creation of a strong bond between a metal atom and a light element atom such as boron or hydrogen.

A two-dimensional nucleation - 2D mode of Frank-van der Merwe can be realized and the formation of nanowires comes as a result.

The Ni-B, H bond strength will be greater than the Ni-Ni bond strength:

$$\varphi_{Ni\text{-}Ni} < \varphi_{Ni\text{-}B,\, H}$$

Influence of different supports on the formation of nanosized materials

Figures 7 to 9 present SEM micrographs of Ni nanowires obtained by the borohydride reduction in $NiSO_4$ water solutions on different supports, weight Ni/support ratio = 1 and B - variant of support wetting procedure. Three different mesopore ceramic supports (SiO_2, SiMCM, AlMCM) with various SSA were used.

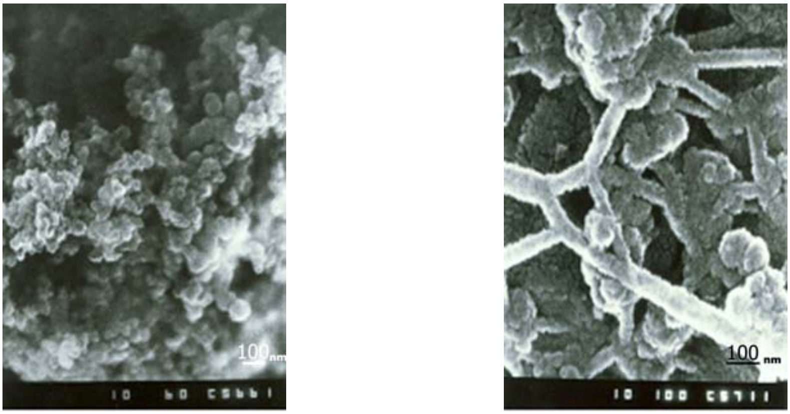

Fig.7. SEM micrograph of: a) SiO_2 support, b) NiB/ SiO_2 nanowires obtained from $NiSO_4$ on SiO_2 support, SSA=32.14 m^2/g, Ni/SiO_2 = 10, B-wetting procedure.

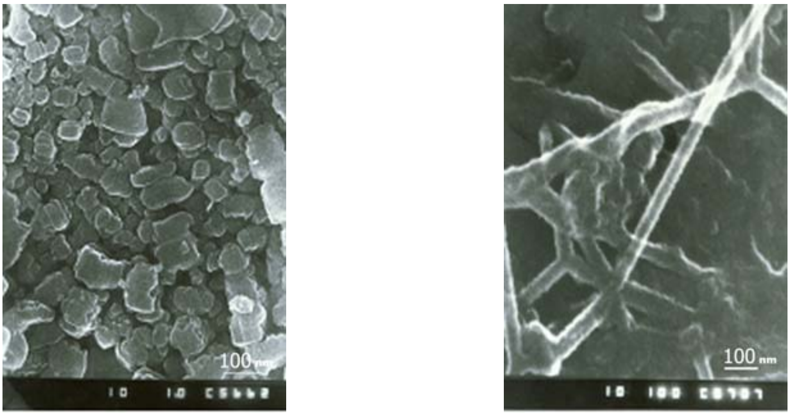

Fig.8. SEM micrograph of: a) SiMCM support, b) NiB/ SiO_2 nanowires obtained from $NiSO_4$ on SiMCM support, SSA=35.90 m^2/g, Ni/SiO_2 = 10, B-wetting procedure

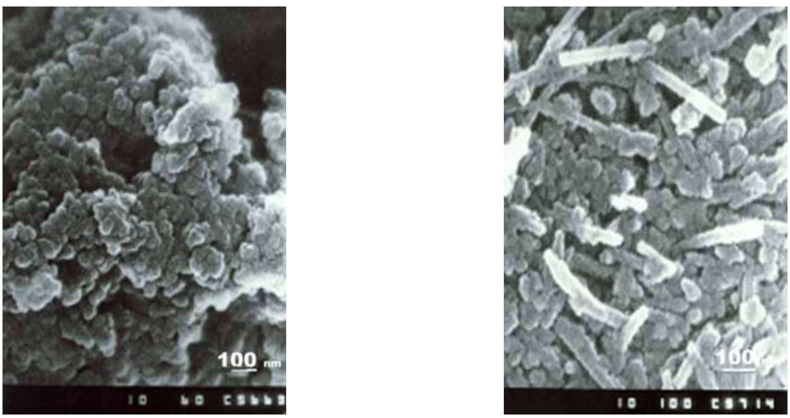

Fig.9. SEM micrograph of a) AlMCM support, b) NiB/ SiO_2 nanowires obtained from $NiSO_4$ on AlMCM support, SSA=42.56 m^2/g, Ni/SiO_2 = 10, B-wetting procedure.

The supports affect the mechanism of formation of the isotropic, respectively anisotropic by shape nanostructures (nanoparticles or nanowires) via the chemical nature (element content), the inserted quantity (as a ratio to Ni) and the grain size (SSA) [4,5].

The support assists the formation of nanowires with highly developed SSA, which becomes the focal point for meeting and bonding of Ni, B and H atoms forming nanowires.

With increasing of SSA supports, the SSA nanowires increase too, while the nanowires diameter decreases.

The Table below presents the data for the different supports and the obtained nanowires.

Tab.1. Data for the supports and nanowires.

$SSA_{support}$ [m^2/g]	$SSA_{nanowires}$ [m^2/g]	$Diameter_{nanowires}$ [nm]
SiO_2 - 189	32.14	90
SiMCM - 349	35.90	50
AlMCM - 307	42.56	40

In the case of the use of AlMCM support, a mixed phase of nanowires and nanoparticles has been formed.

Composition and specific surface area (SSA) of synthesized nanostructured materials

In Table 2 the experimental data for the composition (the content of Ni and B and the support quantity) and SSA of the synthesized nanowires and nanoparticles obtained from $NiSO_4$ and $NiCl_2$ water solution and A-variant of support wetting procedure are given.

Tab.2. Experimental data for the Ni nanoparticles and nanowires composition.

Precursor salt	Weight ratio Me/support	SSA [m^2/g]	Boron(B) [Wet. %]	Ni [Wet. %]	Support SiO2 [Wet. %]
$NiSO_4$	10	32.14	3.23	81.48	15.29 - A
$NiSO_4$	10	35.92	3.71	84.92	10.75 – A SiMCM
$NiSO_4$	10	42.56	3.99	89.566	3.44 – A AlMCM
$NiSO_4$	1	59.23	3.00	39.30	56.76 - A
$NiSO_4$	0.6	67.18	3.21	28.56	67.79 - A
$NiSO_4$	0.4	104.28	2.80	19.72	77.44 - B
$NiSO_4$	0.3	109.41	1.97	13.98	84.05 - B
$NiCl_2$	1	72.85	3.50	33.86	62.49 - A

It can be seen that the support chemical nature affects the Ni quantity and the SSA of the obtained nanowires, as well as that the weight Ni/support ratio also determines the deposited Ni and boron quantity.

With a decreasing of Ni/support ratio from 10/1, i.e. with increasing of the SiO_2 support quantity, the SSA of the nanostructures obtained from a $NiSO_4$ water solution on SiO_2 support and A - wetting variant increases from 32.14 m^2/g to 59.23 m^2/g, while the Ni and B quantities decrease.

The B-wetting variant affects the SSA and the Ni and B quantities in the same way. With a decreasing of the weight Ni/SiO_2 ratio (from 0.4/0.3) the Ni and B quantities decrease as well, but the SSA increases much more than in the case of A-wetting variant (from 104.28 to 109.41 m^2/g), consequently the nanoparticle quantity increases compared to the A-wetting procedure.

XPS data

Both the chemical elements content on the nanostructures surface and the binding energy of electrons from different quantum levels were determined by XPS.

Figure 12 presents the spectrum of B1s electrons having a binding energy BE = 192 eV, while Figures 10 and 11 present the spectra of Ni 2p and Ni 3s electrons having binding energies, respectively BE = 856 eV and BE = 113 eV.

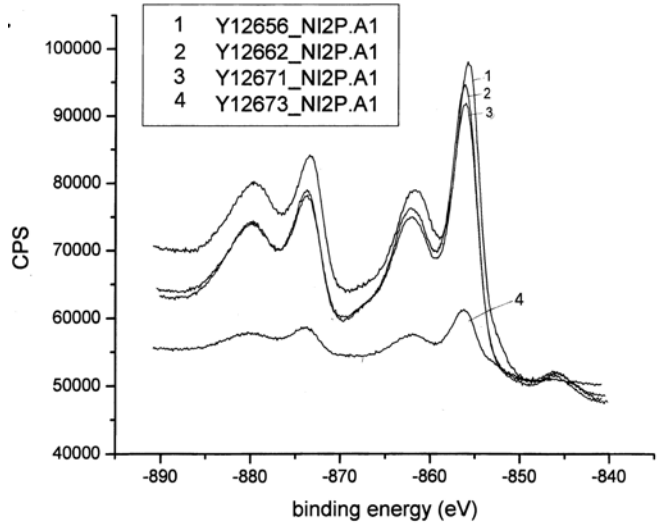

Fig.10. XPS spectrum of Ni2p electrons.

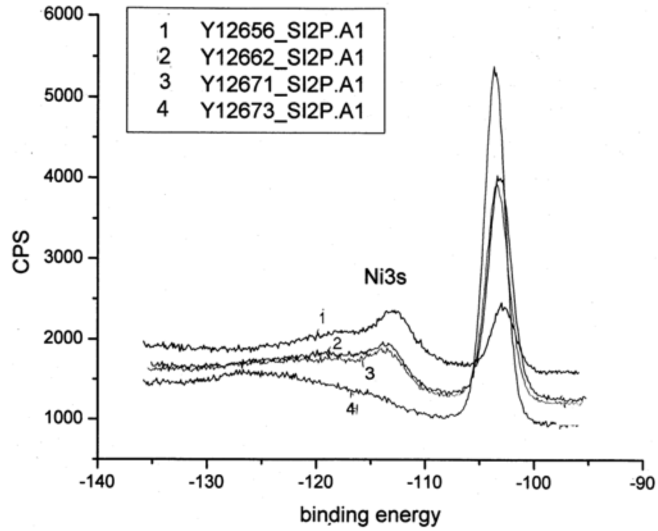

Fig.11. XPS spectrum of Ni3s electrons.

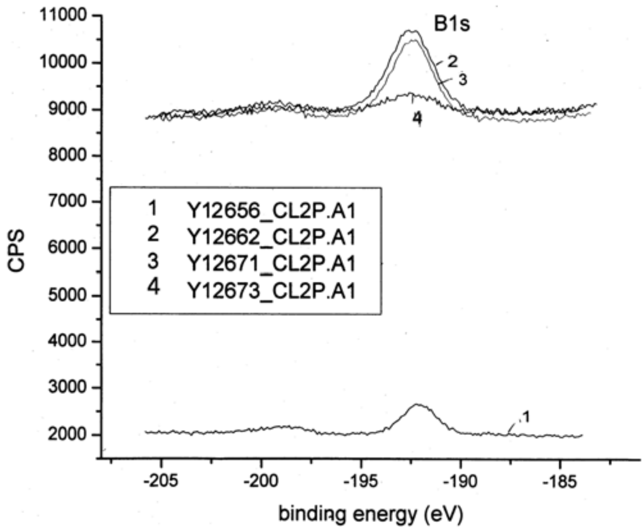

Fig.12. XPS spectrum of B1s electrons.

CONCLUSION

Nanowires and nanoparticles have been synthesized from various aqua Ni salt solutions ($NiSO_4.6H_2O$, $NiCl_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and $NiBr_2.3H_2O$) by the borohydride reduction method and on different supports.The anion content of the Ni complexes is of importance for the nucleation of either isotropic or anisotropic by shape nanosize materials. The two-element anions (SO_4, NO_3) determine the nanowire formation, while the single-element anions (Cl, Br) form nanoparticles.The mesopore ceramic support affects the mechanism of formation of isotropic or anisotropic by shape nanostructures via chemical nature (element content), the inserted quantity (as a ratio to Ni) and the grain size (SSA).The wetting procedure of the support surface is also of special importance. The introduction of support with Ni salt solution to the reducing agent is more suitable for nanowire formation. The grain size (a diameter from 40 nm to 140 nm) and the quantity of the nanoparticles and nanowires are directly dependent on the Ni/support ratio.

Acknowledgements

The authors gratefully acknowledge support from NENAMAT - CONSORTIUM and the National Science Fund at the Ministry of Education and Science – Bulgaria. They are thankful for the financial help for the obtaining and investigation of nanomaterials in this report.

REFERENCES

[1] Kida, A., Kajiama, H., Hashizume, T., Koike, k.: Applied Physics Letters, vol. 75, 1999, no. 4, p. 540
[2] Yu-Ying, Ser-Sing Chang, Chien-Liang Lee, Chris Wang, CR.: Journal of Physical Chemistry B, vol. 101, 1997, no. 34, p. 6661
[3] Yong-Jin Han, Ji Man, Stucky, D.: Chemistry of Materials, 2000, no. 12, p. 2068
[4] Wei-Jiang Wang, Ming-Hua Qiao, Jun Yang, Song-Hai Xie, Jing-Fa Deng: Applied Catalisis A: General, vol. 168, 1998, p. 101
[5] Wei-Jiang Wang, Ming-Hua Qiao, He-Xing Li, Wei-Lin Dai, Jing-Fa Deng: Applied

Catalisis A: General, vol. 168, 1998, p. 151
[6] Jana, NR., Gearheard, L., Murphy, C.: Chemical Communications, 2001, p. 617
[7] Metzeger, R., Konovalov, V., Sun, M., Xu, T., Zangari, G., Xu, B., Benakli, M., Doyle, W.: IEEE Transactions on Magnetics, vol. 36, 2000, no. 1, p. 30
[8] Dragieva, I., Ivanova, G., Klabunde, K.: Scripta Materialia, vol. 44, 2001, p. 2187
[9] Dragieva, I., Ivanova, G., Bliznakov, S., Lefterova, E., Stoynov, Z., Markova-Deneva, I., Pankova, M.: Physical Chemical Glasses, vol. 41, 2000, no. 5, p. 264
[10] Alexandrova, K., Markova-Deneva, I., Vassilev, S., Dragieva, I. In: Proceedings of the 4th Workshop Nanoscience and Nanotechnology Nanostructured Materials Application and Innovation Transfer, October 2002. Ed. E. Balabanova, I. Dragieva. Heron Press Ltd., 2003, issue 3, p. 67
[11] Alexandrova, K., Markova-Deneva, I., Gigova, A., Dragieva, I. In: Proceedings of the 5th Workshop Nanoscience and Nanotechnology Nanostructured Materials Application and Innovation Transfer, November 2003. Ed. E. Balabanova, I. Dragieva. Heron Press Ltd., 2004, issue 4, p. 52
[12] Alexandrova, K., Markova-Deneva, I., Popova, M., Mavrodinova, V., Stoycheva, M., Gigiva, A., Dragieva, I.: Journal of the University of Chemical Technology and Metallurgy, vol. 4, 2004, p. 1031
[13] Alexandrova, K., Markova-Deneva, I., Dragieva, I., Stoycheva, M., Vassilew, S., Gigova, A., Iliev, TZ. In: Proceedings of the 6th Workshop Nanoscience and Nanotechnology Nanostructured Materials Application and Innovation Transfer, October 2004. Ed. E. Balabanova, I. Dragieva. Heron Press Ltd., 2005, issue 5, p. 50