

## Technology For High-Temperature Tantalum Carbide Coatings

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**ABSTRACT:-** Ion-plasma sputtering and codeposition of ultrafine tantalum and carbon particles were used to prepare the specimens of coatings in the concentration range of 4.6-71.5 at.% C. The study of the structure found the existence of the carbon solid solutions with up to 4.6 at.% C in the  $\beta$ -tantalum, the carbon solid solutions in the  $\alpha$ -tantalum at 4.6-10.3 at.% C and direct synthesis of TaC at 44.7-71.5 at.% C. The heat treatment up to 700 °C causes a significant expansion in concentration of the regions of Ta<sub>2</sub>C and TaC existence. Electron microscopic studies confirmed the absence of defects (cracks or voids) in the tantalum carbide coatings. The possibility of tantalum carbide TaC direct synthesis application in mechanical engineering is noted.

**Keywords:-** tantalum, carbon, magnetron, direct synthesis, tantalum carbide

### I. INTRODUCTION

Cubic tantalum carbide TaC is characterized by unique performance properties, which depend on the carbon content. The melting point of non-stoichiometric carbide TaC<sub>0.88</sub> is 4250 K, the microhardness is H<sub>V</sub> TaC<sub>0.85</sub> - 29.0 GPa [1]. At the moment, there are several technologies available for preparation of tantalum carbide [2]; each is carried out at high temperature:

- Recovery of tantalum oxide with carbon, followed by formation of carbide. Recovery of Ta<sub>2</sub>O<sub>5</sub> and subsequent formation of tantalum carbide is carried out at the temperature of 1400-1600 °C in hydrogen or in a vacuum. The source of carbon is the carbon black.
- Direct saturation of tantalum by carbon. In this case, the technology for tantalum carbide preparation is similar to the above method, but here the oxide is replaced by metal tantalum. The modification of this method suggests preparation of tantalum carbide in the graphite crucible containing tantalum, carbon, aluminum melt or other iron group metals instead of aluminum at the temperatures up to 2000 °C. The resulting product is treated with acid to dissolve the formed side carbides of aluminum or iron.
- Deposition from the gas phase. The method is based on the process of five-chloride tantalum recovery at the surface of tungsten or carbon filament to the tantalum which interacts with hydrocarbon medium at the temperatures 2000 °C - 2930 °C
- Recovery melting of tantalum-containing slag. Recovery and carbidization of tantalum occurs as the result of carbon addition in the slag in a large excess and presence of iron. The resulting carbide is recovered chemically.

Therefore, the development of single-stage technology for tantalum carbides preparation at the room temperature in the form of coatings on the products has determined the interest for industrial application.

In accordance with the existing equilibrium phase diagram [3, 4], the system is characterized by the presence of two-carbides: TaC<sub>1-x</sub> and TaC<sub>2</sub>. The TaC<sub>2</sub> phase has two crystallographic modifications:  $\alpha$  and  $\beta$ . The  $\zeta$ -Ta<sub>3</sub>C<sub>2</sub> carbide can exist in the system.

At the same time, the development of ion-plasma technologies of materials forming with the flows of ultrafine sputtered metals particles provides the possibility of preparing the materials, combined with application of film coatings on the products [5]. And the resulting materials have physical properties that significantly differ from those of bulk samples [6-9]. Significant changes occur in the structure of materials prepared by coprecipitation of sputtered particles, the concentration regions of solid solutions (SS) increase. The latter can be explained from the view point of thermofluctuational melting of small particles [10, 11], when the existence of small particle in a quasi-liquid state is limited to a certain maximum size above which thermofluctuation conditions are excluded.

The purpose of this paper is to describe the single-stage technology for preparation of tantalum carbides coatings at the room temperature with a wide range of carbon content variations.

## II. EXPERIMENTAL

The tantalum of 99.96 wt. % as the basic element and the purified graphite were used in the experiments. These materials were used to prepare the magnetron targets 40 mm in diameter and 4 mm thick. Argon used as the plasma-forming gas during magnetron sputtering was purified with a sputtered titanium getter.

Samples of coating were prepared by the procedure consisting in the magnetron sputtering of tantalum and carbon and their cooperative deposition on the polycore (polycrystalline corundum  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) substrate that is movable with respect to plasma steams. The coatings were prepared in the form of short-period sublayers 1 nm thick that form films 1÷1.5  $\mu$ m. The velocity of substrate movement was  $5 \cdot 10^{-2}$  m·s<sup>-1</sup>. The sputtering was performed with the simultaneous use of two magnetrons located opposite one another; the spacing between magnetrons was separated by a unit for substrates moving. The temperature of the coating during formation was maximum 100 °C. Annealing of the samples was performed in a high temperature vacuum electric furnace at the pressure of  $1 \cdot 10^{-2}$  Pa.

The composition of coatings was controlled by varying the powers supplied to magnetrons sputtered tantalum and graphite targets. The proportion of deposited elements was checked by the weighing technique, i.e. by determining the amounts of elements sputtered and deposited during the formation of coating. The film thickness was measured by the Rutherford backscattering of protons in the tandem accelerator UKP-2-1. The X-ray diffraction studies were performed using a D8 Advance (Bruker) diffractometer with copper radiation  $\lambda_{\text{Cu}} = 0.154051$  nm and a graphite monochromator. The lattice parameters were determined by averaging magnitudes obtained in using all diffraction reflections of identified phase. Electron-microscopic studies were performed using a JSM-8230 (JEOL) electron microprobe analyzer.

## III. RESULTS AND DISCUSSIONS

As the result of the studies we prepared the tantalum-carbon films of 12 compositions from 4.6 to 71.5 at. % carbon and performed the X-ray structural analysis of the prepared samples. Table 1 shows the phase and elemental compositions and the partial thickness of tantalum ( $d_{\text{Ta}}$ ) and carbon ( $d_{\text{C}}$ ) layers during coatings preparation.

**Table 1. Process parameters of coating preparation, the partial thickness of tantalum and carbon layers during coatings formation and carbon concentration in the coatings.**

$W_{\text{Ta}}$ , Wt	$W_{\text{C}}$ , Wt	$d_{\text{Ta}}$ , nm	$d_{\text{C}}$ , nm	Carbon concentration $C_{\text{C}}$ , at. %	phases
80	10	1.01	0.02	4.6	$\beta$ -Ta
80	24.2	1.00	0.04	10.3	amorph
80	50	0.97	0.08	18.7	amorph
53.7	50	0.66	0.09	26.9	amorph
39	50	0.54	0.09	31.5	amorph
30	50	0.42	0.08	35.8	amorph
25	50	0.35	0.08	38.3	TaC + Ta <sub>4</sub> C <sub>3</sub>
20	50	0.29	0.08	44.7	TaC + Ta <sub>4</sub> C <sub>3</sub>
15	50	0.21	0.07	51.6	TaC
10	50	0.16	0.07	55.8	TaC
8	50	0.12	0.07	63.1	TaC
5	50	0.08	0.07	71.5	Amorph TaC + amorph C

Fig. 1 shows the diffraction patterns of the most characteristic samples after sputtering on the polycore substrates. We can see that the coating with 4.6 at. % C (Fig. 1, spectrum 1) is represented by strongly textured in [002]  $\beta$ -tantalum. Since there are no reflections from the  $\beta$ -tantalum except the reflexes with Miller indices (002) and (004), it is not possible to calculate the parameters of the tetragonal lattice of this phase. With carbon content of 10.3 at.% in the coating we obtained the solid solution of carbon in  $\alpha$ -tantalum. Further, the coating with the carbon content in the range of 10.3-35.8 at. % was amorphized (Fig. 1, spectrum 2). The value 2.2 nm was obtained in calculation of crystallites sizes from the broadening of the diffraction peaks with the help of WinFit! software [12]. Starting from carbon content of 38 at.% up to the content of 45 at.% C the coating is represented by the tantalum carbide TaC phase with a fcc lattice with the parameter  $a = 0.4417 \pm 0.0017$  nm (Fig. 1, spectrum 3).

In the range of carbon content from 50 to 63 at. % (Fig. 1, the spectrum 4), the coating is presented by tantalum carbide TaC phase, the lattice parameter varies from  $a = 0.4428 \pm 0.0011$  nm for the composition of

51.6 at. % C to  $0.4445 \pm 0.0002$  nm for the composition of 63.1 at. % C. The coating with the carbon content of 71.5 at. % was amorphized (Fig. 1, the spectrum 5), which was confirmed by a small halo  $2\theta = 30$ -35 degrees.

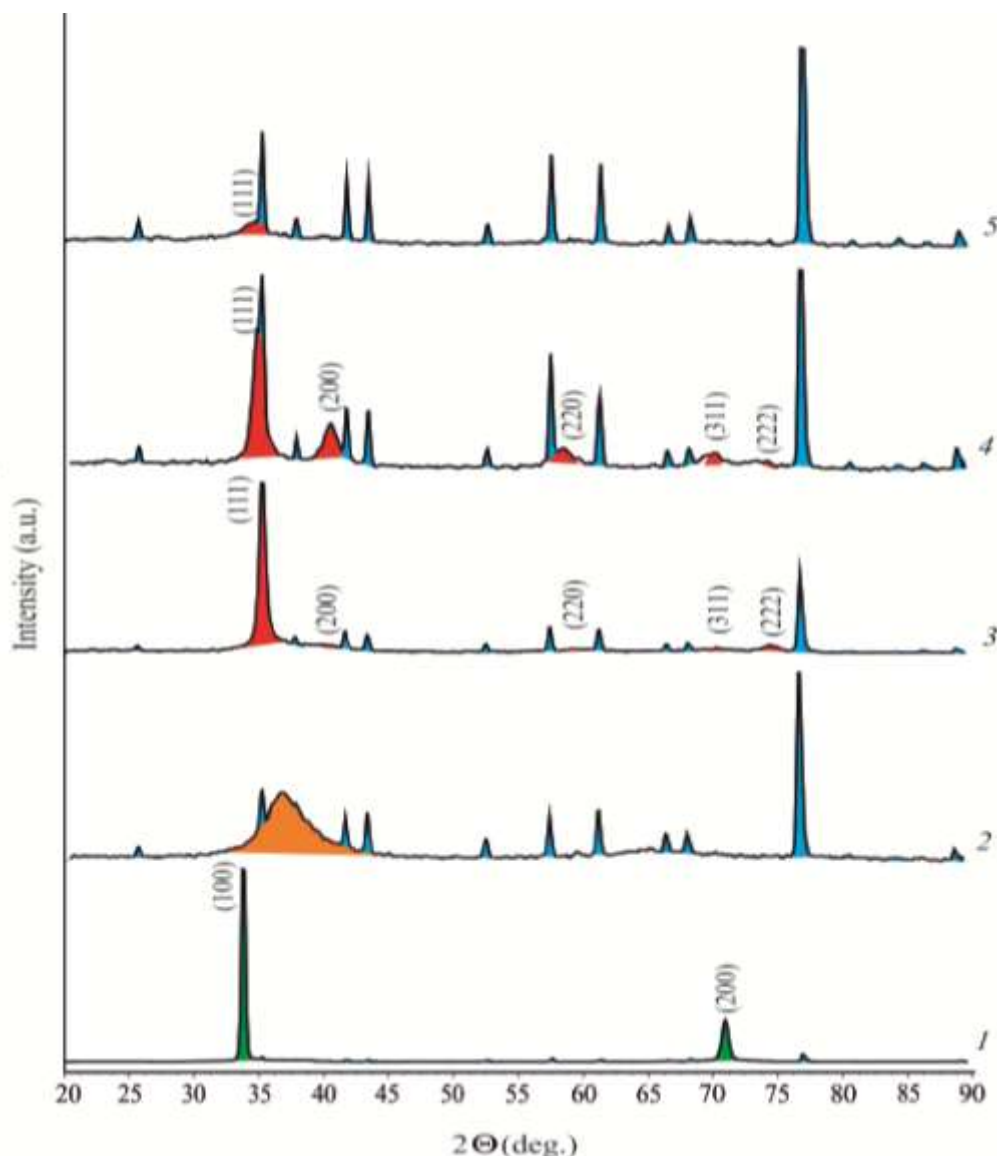


Fig. 1. Diffraction patterns of tantalum-carbon film coatings with carbon concentration, % (at.): 1 – 4.6; 2 – 26.9; 3 – 44.7; 4 – 55.8; 5 – 71.5; ■ -  $\beta$ -Ta; ■ - TaC; ■ – amorphous phase; ■ -  $\alpha$  -  $\text{Al}_2\text{O}_3$  (substrate);

The vacuum annealing of the tantalum-carbon system was performed at 300, 400, 500, 600 and 700 °C for 1 hour to determine the thermal stability boundaries of the resulting coatings. The annealing at 300 °C showed no structural changes in the samples. But the samples with the formation of tantalum carbide TaC phase, recorded during sputtering, show the change in the  $a$  parameter of the fcc lattice of this phase after annealing. Table 2 shows the  $a$  parameter values for the TaC phase fcc lattice under the change of the annealing temperature for various initial coating compositions. We assume that the excess (in relation to the stoichiometry) carbon was released from the TaC phase in the form of graphene nanoplates, as revealed in [14]. But, unfortunately, we do not have such equipment for direct observation of the nanoplates.

We can see from Table 2 that the sample with carbon content of 38.3 at.% after annealing at 300 °C has no signs of TaC phase and it remains amorphous after 400 °C. Thus, the TaC phase at this carbon concentration falls in favor of  $\text{Ta}_2\text{C}$  phase more stable under these conditions. The coating with 44.7 at. % C is the most fragile and the thermocycling resulted internal stresses destroyed it after the heat treatment at 600 °C.

Table 2. Dependence of  $a$  parameter (nm) TaC phase fcc lattice for various compositions after annealing at different temperatures.

Annealing temperature, °C	Carbon concentration in initial coatings, at. %:					
	38.3	44.7	51.6	55.8	63.1	71.5
No annealing	$a=0.4367$ $\pm 0.0021$	0.4417 $\pm 0.0017$	0.4428 $\pm 0.0011$	0.4446 $\pm 0.0008$	0.4445 $\pm 0.0002$	-
300	-	0.4402 $\pm 0.0018$	0.4415 $\pm 0.0014$	0.4447 $\pm 0.0015$	0.4436 $\pm 0.0005$	-
400	-	0.4420 $\pm 0.0040$	0.4415 $\pm 0.0007$	0.4442 $\pm 0.0007$	0.4430 $\pm 0.0007$	0.4480 $\pm 0.0047$
500	-	0.4402 $\pm 0.0037$	0.4413 $\pm 0.0015$	0.4439 $\pm 0.0004$	0.4421 $\pm 0.0006$	0.4460 $\pm 0.0065$
600	-	0.4380 $\pm 0.0022$	0.4403 $\pm 0.0012$	0.4433 $\pm 0.0007$	0.4415 $\pm 0.0008$	0.4441 $\pm 0.0033$
700	-	Sample crumbled	0.4402 $\pm 0.0011$	0.4433 $\pm 0.0005$	0.4422 $\pm 0.0010$	0.4438 $\pm 0.0030$

Annealing of the samples with the carbon content from 10.3 to 38.3 at.% was characterized by formation of Ta<sub>2</sub>C phase. Fig. 2 shows the diffraction pattern of the sample with 38.3 at.% C in the initial state after sputtering (spectrum 1), after annealing at 300 °C and 700 °C (spectra 2 and 3 correspondingly). It is evident that the TaC phase in the initial state coexists with Ta<sub>2</sub>C phase, but after annealing at 300 °C only nanocrystalline phase Ta<sub>2</sub>C remains with the grains so small, that diffusion of the diffraction reflexes does not enable us to calculate the lattice parameters. Annealing at 400, 500 and 600 °C does not lead to noticeable changes of phase composition, and only after 700 °C (Fig. 2, spectrum 3) the structure becomes crystallized in the extent enabling us to calculate the lattice parameters.

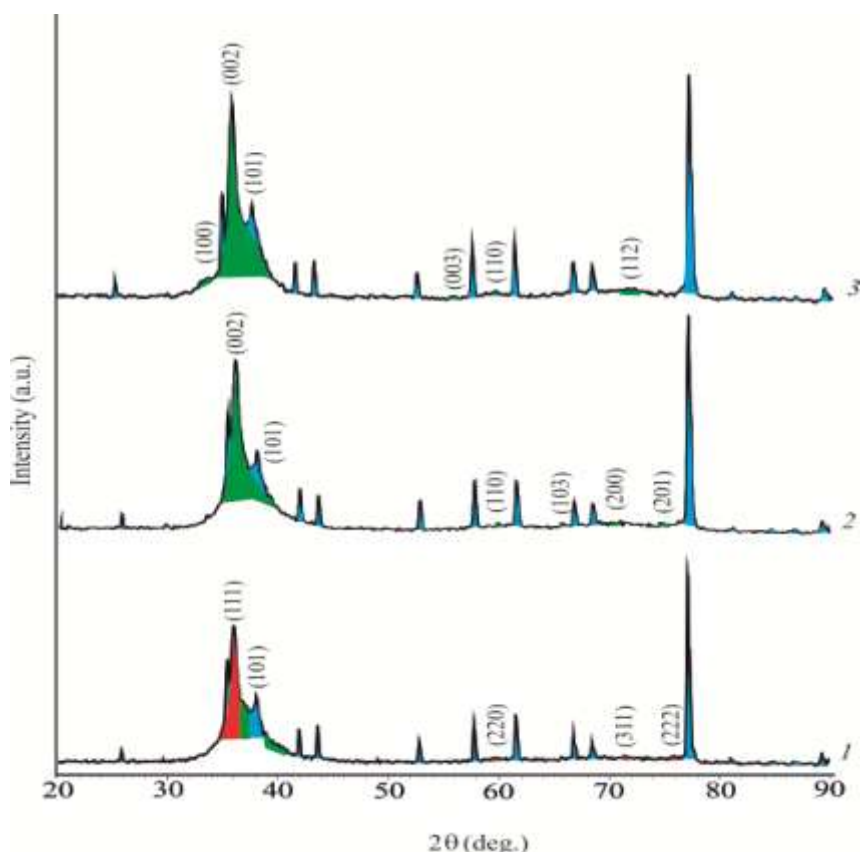


Fig. 2. Diffraction patterns of the coating with carbon content 38.3 at. %: 1 – no annealing, 3 – annealing at 300 °C for 1 hour, 3- the same at 700 °C; ■ - TaC; ■ - Ta<sub>2</sub>C; ■ -  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (substrate).

The calculation made in the Index software [13] provided the values  $a = 0.3108$  and  $c = 0.4949$  nm, which are close enough to its table values (card JC PDS №73-1321:  $a = 0.3103$  and  $c = 0.4937$  nm).

The electron-microscopic studies performed using the electron microprobe analyzer JSM-8230 (JEOL) showed that the coatings both at the micro and meso level are free of defects, which could affect their protective properties. Fig. 3 shows the micro images of the coating with 55.8 at.% C.

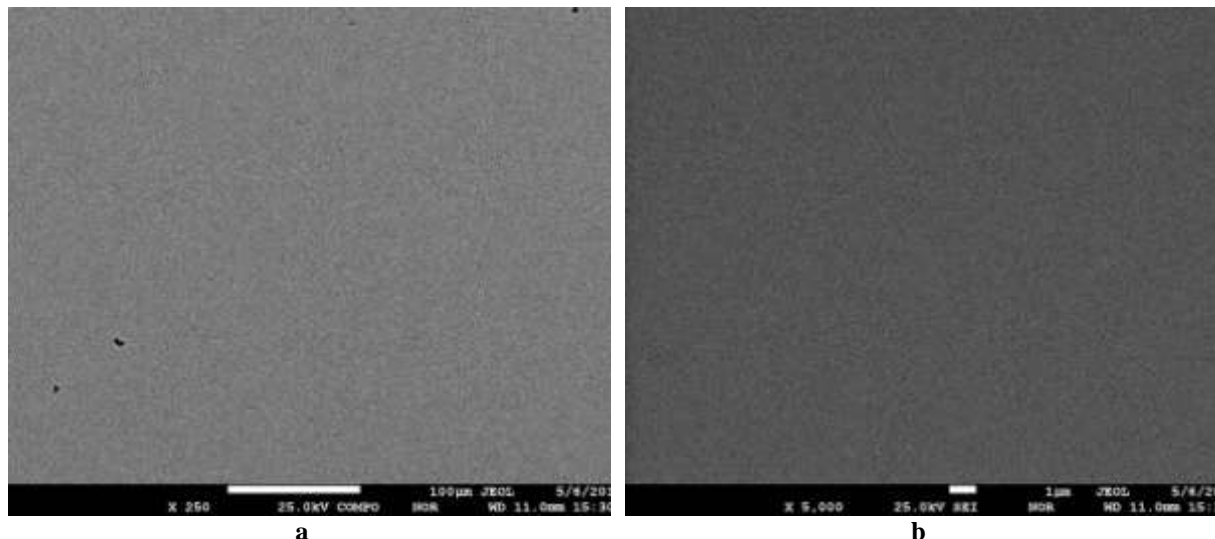


Fig. 3. Micro images of the tantalum carbide coating with 55.8 at.% C, with magnification  $\times 250$  (a) and  $\times 15000$  (b)

The studies of the TaC coatings with other carbon concentrations confirm the lack of visible defects: cracks and voids.

#### IV. CONCLUSION

Thus, it is shown that the direct synthesis of tantalum carbide directly in the process of simultaneous deposition of tantalum and carbon in the form of nanolayers indicates that the sputtered carbon behaves like the gas components during the reactive ion-plasma sputtering. The significant concentration expansion of the homogeneity area of  $\alpha$ -Ta<sub>2</sub>C and TaC carbides was noted. Thus, the field of tantalum monocarbide TaC ranges from 44.7 to 71.5 at.% C. The reason for the absence of carbon phase traces in the diffraction patterns can be much lower reflectivity of the carbon phases compared with TaC and Ta<sub>2</sub>C.

Thereby, the formation of coatings as in the example of tantalum-carbon system by the ultra-dispersed particles can significantly change the structure and properties of the resulting materials. We should mention the possibility of using the technology of direct TaC tantalum carbide synthesis in the machine engineering to improve the performance characteristics of the machine parts operating in extreme conditions.

#### REFERENCES

- [1]. Gusev A.I., Rempel A.A. Nonstoichiometry, disorder and order in solids. Ural Branch of RAS, Ekaterinburg (2001). 580 p.
- [2]. Kosolapova T.Y. Carbides. Metallurgy, (1968). 300 p.
- [3]. Barabash O.M., Koval Yu.N. Crystal structure of metals and alloys. Kiev: Naukova Dumka, 1986. 598 p.
- [4]. The diagrams of binary metallic systems. Ed. Lyakishev N.P. M.: Machine engineering, 1996. V.1. 992p.
- [5]. Volodin V.N., Tuleushev Yu.Zh., Zhakanbaev E.A. The structure and phase composition of deposited niobium-carbon films. The Physics of Metals and Metallography, (2013); 114, 432-437
- [6]. Volodin V.N., Tuleushev Yu.Zh., Tsai K.V., Zhakanbaev E.A. The new phase Mo<sub>3</sub>Pb with A15 structure in solid solutions of molybdenum-lead film system. The Physics of Metals and Metallography, (2014); 115, 532-538.
- [7]. Tuleushev Yu.Zh., Volodin V.N., Zhakanbaev E.A. Nanosized copper-doped coatings of beta-tantalum: preparation, structure and properties. The Physics of Metals and Metallography, (2013); 114, 625-632.
- [8]. Volodin V.N., Tuleushev Yu.Zh., Zhakanbaev E.A. The structure of  $\beta$ -tantalum-tungsten alloys films produced by co-precipitation of sputtered metals. Surface, (2014); 8, 1146-1151.
- [9]. Tuleushev Yu.Zh., Volodin V.N., Zhakanbaev E.A. The tantalum-cadmium film coatings: preparation, phase composition and structure. The Physics of Metals and Metallography, (2015); 116, 59-66.
- [10]. Skripov V.P., Koverda V.P. Spontaneous crystallization of the supercooled liquids. Nucleation of crystals in liquid and amorphous solids. M.: Science, 1984. 232 p.
- [11]. Roduner E. Size effects in nanomaterials. M.: Technosphere, 2010. 350p.

- [12]. **WinFit! V1.2:** Package for complete profile-analysis of x-ray reflections (profile fitting, size, strain) (S. Krumm, July 1995-97) <ftp://xray.geol.uni-erlangen.de/software/windows/winfit/winfit.zip>.
- [13]. Shelekhov E.V., Sviridova T.A. Programs for X-ray Analysis of Polycrystals. *Metal Science and Heat Treatment*, v.42 (2000), No.8, pp.309-313
- [14]. A. Nieto, A. Kumar, D. Lahiri, Zhang C., Seal S., Agarwal A. Oxidation behavior of graphene nanoplatelet reinforced tantalum carbide composites in high temperature plasma flow. *Carbon*, 67 (2014) 398-408.