Scientific report on the project implementation during January-November 2016

Programul: **IDEI**

Tipul proiectului: **Proiecte de cercetare exploratorie**

Cod proiect: **PCE_ PNII-ID-PCE-2011-3-0522**

Titlul proiectului: **Giga and terra-watt laser interaction with carbon, tungsten and beryllium films »**

Director de proiect: Dr. Cristian P. LUNGU, INFLPR, Magurele

Objectives:

6.1 Thernary mixed film (Be-C-W) interaction with plasma produced by a high power laser (TEWALAS)

Activities:

6.1.1 Be-C-W samples characterization before laser irradiation using the methods: AFM, SEM, XPS, XRD, Raman, TDS.

6.1.2 Be-C-W samples characterization after laser irradiation using the methods: AFM, SEM, XPS, XRD, Raman, TDS.

6.2 Disemination of the results

6.2.1 Preparation and presentation to the 2 Internnational Conferences

6.2.2 Preparation and sending a paper to a scientific journal ISI ranked

6.2.3 Preparation and registration of a brevet to EPO (European Patent Office)

Rezumat in limba romana

In perioada ianuarie-decembrie 2016, au fost abordate si indeplinite activitatile prevazute in cadrul obiectivului 6.1 respectiv studiul interactiei filmelor compozite ternare (Be-C - W) cu plasma produsa in deuteriu de laserul de mare putere (TEWALAS), (ceea ce implica depunerea de filme compozite Be-C-W in configuratie stationara, analiza

acestora), pregatirea si publicarea unur lucrari stiintifice cu cotatie ISI (trei lucrari publicate si una trimisa spre publicare, fata de una singura prevazuta in planul de lucru) si trei prezentari la conferinte internationale, dintre care o lucrare invitata, fata de 2 prezentari prevazute initial). Toate lucrarile si prezentarile au mentionat Acknowledgement pentru sursa de finantare, respectiv Romanian National Authority for Scientific Research, CNCS - UEFISCDI, project number PN-II-ID-PCE-2011-3-0522.

A fost inregistrat un patent la European Patent Office (EPO), cu inregistrare prealabila la OSIM.

ISI papers

1. L. Avotina, A. Marcu, C. Porosnicu, M. Lungu, A. Stancalie, A. G. Ilie, P. C.Ganea, D. Savastru, J. Kalnacs, C. P. Lungu, G. Kizane, S. Antohe, Multi-wavelength laser irradiation of Be-C-W coatings Digest Journal of Nanomaterials And Biostructures Vol. 11, No. 1, January - March 2016, p. 293 - 302
2. L. Avotina; Marcu, A; Lungu, M; Stancalie, A; Grigorescu, C; Ilie, AG; Porosnicu, C ; Mihai, L; Sporea, D ; Lungu; Somacescu; Kizane, G; Savastru; Antohe, S., Power density influence on laser-induced graphite structural modifications, Digest Journal of Nanomaterials and Biostructures, Vol.11 I. 3 p.973-981 2016
3. Liga Avotina, Mihail Lungu, Paul Dinca, Bogdan Butoi, Razvan Ungureanu, Aurelian Marcu, Catalin Luculescu, Claudiu Hapenciuc, Paul C. Ganea, Aleksandrs Petjukevics, Cristian Petrica Lungu, Gunta Kizane and Stefan Antohe, Deuterium Influence on Laser Irradiation of Be-C-W Materials, trimisa la publicare in revista *Fusion Engineering and Design*

Conferences:

1. C.P. Lungu / High power laser irradiation of mixed Be/C/W films used in fusion technology / 16th International Balkan Workshop on Applied Physics (IBWAP), Constanta, Romania, 7-9 , invited
2. A. Marcu, C.Viespe, I. Nicolae, B. Butoi, D.Paul, L.Avotina si C.P.Lungu, Patterned Laser-grown Nanowires for Hydrogen Isotopes Detection with SAW-sensors, 5-9 June 2016, international conference „CIMTEC 2016" Perugia, Italia, poster

3. A. Marcu, L. Avotina, C. Porosnicu , A. Marin, C.E.A. Grigorescu, R.Ungureanu, G. Cojocaru, D. Ursescu, M. Lungu, N. Demitri and C.P. Lungu, Femptosecond Laser Induced sp^3 Bounds and Nanodiamonds Formation in Carbon Materials; 5-9 June 2016, international conference „CIMTEC 2016" Perugia, Italia, poster
4. A. Marcu, L. Avotina, C. Porosnicu, A. Marin, C.E.A. Grigorescu, R.Ungureanu, G. Cojocaru, D. Ursescu, M. Lungu, N. Demitri and C.P. Lungu, Femtosecond Laser Induced sp^3 Bonds and Nanodiamonds Formation in Carbon Materials, Applied Nanotechnology and Nanoscience International Conference – ANNIC 2016, nov 9-16, Barcelona, Spain
5. Bogdan Calin, Catalina Albu, Laura Ionel, Ecaterina Iordanova, Georgi Yankov and Aurelian Marcu" Periodical surface nanostructures induced by femtosecond laser Applied Nanotechnology and Nanoscience International Conference – ANNIC 2016, nov 9-16, Barcelona, Spain

Patents:

1. OSIM: A/00698/03-10-2016, Iradieri cu laseri de putere TW/PW, Authors: C.P.Lungu, C.Porosnicu, I. Jepu, M. Lungu, R. Banici, A. Marcu, C.R. Luculescu, D. Ursescu
2. EPO: EP 16464009/14.10.2016, High power TW/PW laser irradiation, Authors: C.P.Lungu, C.Porosnicu, I. Jepu, M. Lungu, R. Banici, A. Marcu, C.R. Luculescu, D. Ursescu

1. Introduction

In pursuing obtaining high quantities of clean energy by nuclear fusion, one of the most challenging problems is related to the plasma facing materials (PFM). These materials must be capable to withstand bombardment with high energy radiations, neutrons and steady state ion fluxes from the plasma and also to large heat loads (>10 MW/m^2) [1,2]. These conditions will surely lead to chemical and physical sputtering at the interaction of plasma with PFM. Material migration in plasma leads to re-deposition of thin composite films with different properties, which will interact in a dissimilar manner with plasma than the original PFM.

Due to their properties, beryllium (Be) and tungsten (W) coated Carbon Fiber Composites (CFC) have been suggested to be used in next-generation fusion devices like ITER [3]. This PFM configuration is already tested at Joint European Torus(JET). For different radiation wavelengths [4], power densities [5] and respectively plasma parameters, interaction processes with Be- C-W layers is an important issue which is not yet completely understood [6,7]. To address this issue Be-C-W composite layers with various atomic ratios were obtained using the Thermionic Vacuum Arc technology (TVA) [8-10]. The layer thickness was ~400 nm, similar with the one encountered in JET [11]. The Be-C-W composite films were exposed to laser irradiation from a terawatt Ti: Saphire laser system, ~100 fs pulse duration in single pulse and multi-pulse mode [12]. Two different irradiation scenarios were used. First irradiation in low pressure deuterium atmosphere to simulate the interaction in a working nuclear fusion reactor and the second in atmospheric air in a loss of vacuum scenario. Laser induced changes in the morphology was studied by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), and sample composition and bonds were studied by Energy Dispersive Spectrometry (EDS), of X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy.

2. Experimental

Be-C-W mixed layers were deposited using (TVA) technology [13, 14]. The experimental set-up used for this study is illustrated in Fig 1 and is composed of three individual anode-cathode systems. Fig. 2 shows the samples distribution on the holder.

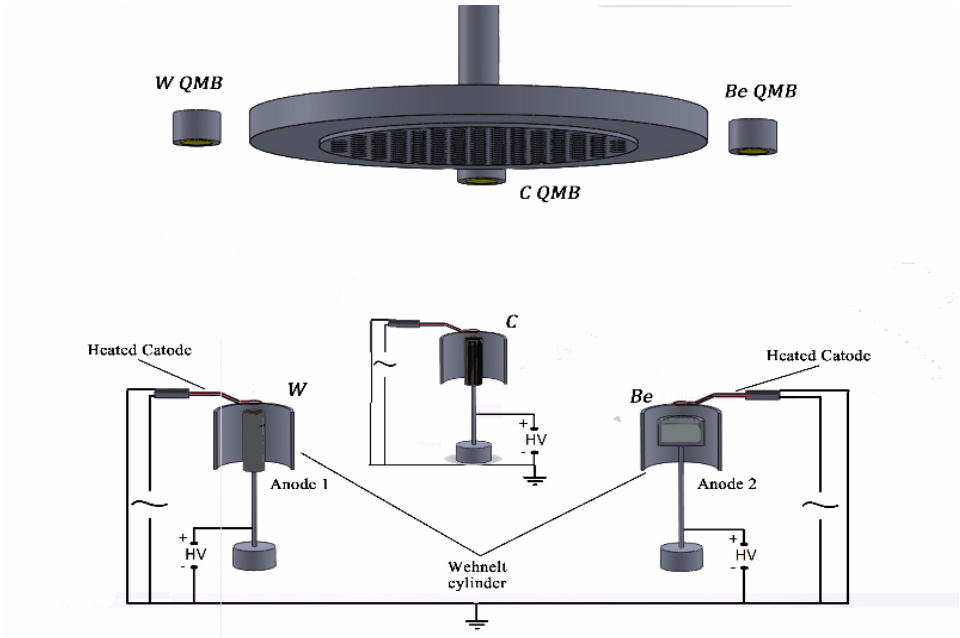


Fig. 1 TVA deposition system experimental setup

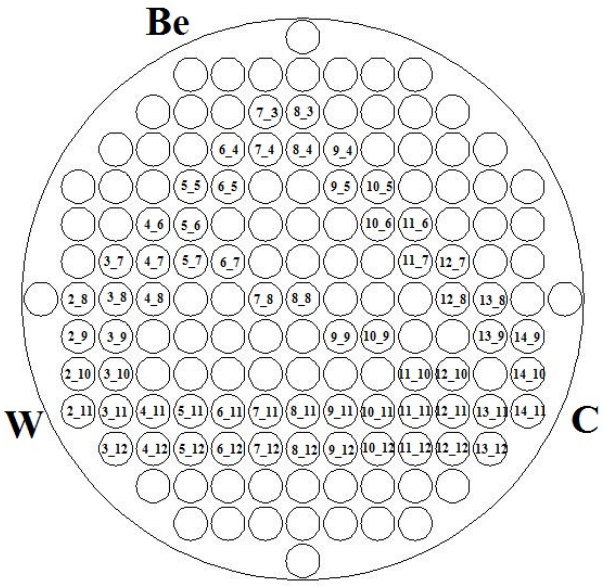


Fig. 2 Samples distribution on the holder using 3 TVA evaporators.

Deposition rates and thickness were monitored in-situ for beryllium and tungsten using a quartz micro-balance system. This allowed to obtain the desired Be-W atomic

ratio 9:1 and a total thickness of 400 nm. Deposition rates were 0.04 nm/s for W and 0.11 nm/s for Be and for C were estimated at 0.1 nm/s based on previous calibrations. In detail, the every evaporator parameters are: i) carbon**:** $d_{C\text{-}QMB}$ = 25 cm, $d_{C\text{-}sample}$ =24 cm, $f_{Correction} = (25/24)^2$ = 1,085, U_d (V) = 890 V, I_d (A) = 1.8 A, deposition rate = 1,6 nm/s, thickness = 250 nm, deposition time = 5 min, residual pressure = P = 1.4 x 10^{-5} torr; ii) tungsten: $d_{W\text{-}QMB}$ = 36.5 cm, $d_{C\text{-}sample}$ =23 cm, $f_{Correction} = (36.5/23)^2$ = 2.51, U_d (V) = 2300 V, I_d (A) = 1.9 A, deposition rate = 0.51 nm/s, thickness = 280 nm, deposition time = 125 min, residual pressure; P = 6.5 x 10^{-6} torr; iii) beryllium: $d_{Be\text{-}QMB}$ = 25 cm, $d_{C\text{-}sample}$ =22 cm, $f_{Correction} = (25/24)^2$ = 1,54, U_d (V) = 1250 V, I_d (A) = 1 A, deposition rate = 2.72 nm/s, thickness = 500 nm, deposition time = 184 sec, residual pressure; P = 5 x 10^{-6} tor

Samples were irradiated with a high power laser in ambient condition (room temperature, air) and respectively in deuterium (~ 20 Torr). A generic scheme of the experimental setup is presented in Fig. 3. Laser is focused over the substrate surface, but the substrate is not perpendicularly oriented, as could be seen in Fig. 3. The focal spot size is about 0.5 micrometers and is approximatively positioned on the target surface, but the incident angle is estimated at few to several degrees (~ 5^0). Laser repetition rate is 10 Hz while pulse duration is about 100 fs. Pulse energy was of about 4 mJ, while the number of pulses was between 1 to 1000 pulses.

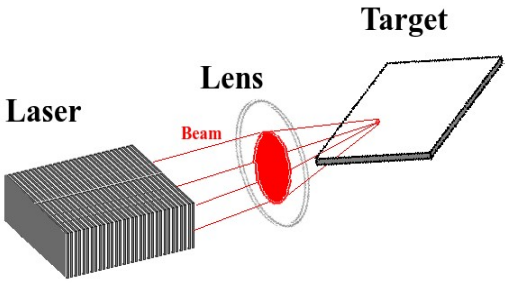
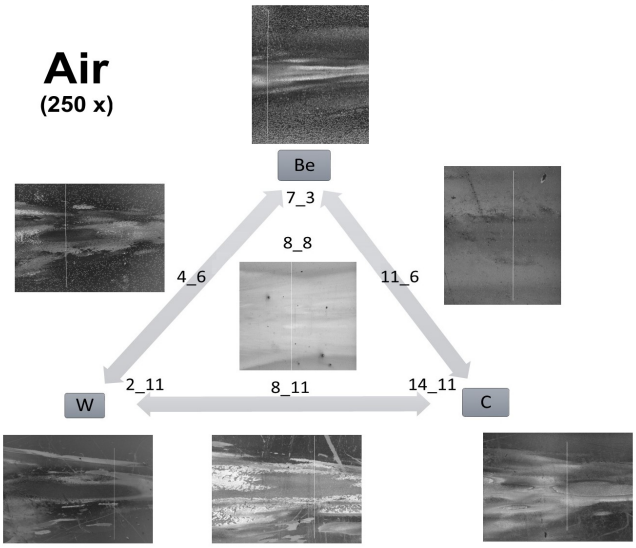


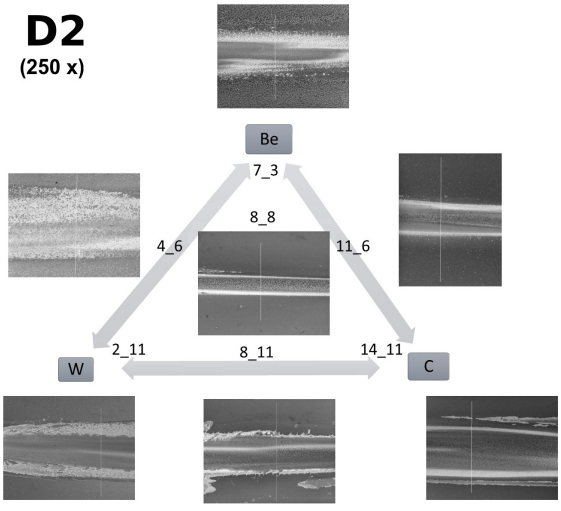
Fig. 3 Experimental setup of laser irradiation system

Scanning Electron Microscopy (SEM) was performed for 100 pulses irradiated zones. The affected zone size changes with respect of sample composition but also with the ambient gas. It could be noticed that Carbon rich zones tend to be wider, but also that

deuterium presence enlarge all ablated areas, and the (partially) affected zones observed in air (Fig. 4a) are more clearly affected in the presence of deuterium (Fig. 4b), The result is a more clear delimitation of the affected area and a wider central affected (ablated) zone. In all cases the ablation process takes place (mostly) in the center of the irradiation zones.



a)



b)

Fig. 4. SEM images of ablated zones in: a) air and b) in deuterium

EDX investigations (performed on the same SEM machine) gives us some supplementary information on the composition of the irradiated zones. As could be observed in Fig. 4 a, carbon and Be are easier (faster) ablated then W. Beside the ablation process enhancement shown by the broadening of the W reach zones (associated with the ablated zones) it could be observed a wider broadening of the carbon reach zones, suggesting the carbon as the fastest removed element particularly in the presence of the deuterium gas. Interesting to remark that in air is less evident such process. Since the beam profile is not a uniform one and the energy tends to decrease on the periphery, this suggests that the ablation threshold is somehow decreasing in the presence of the deuterium as the ambient gas.

a)

b)

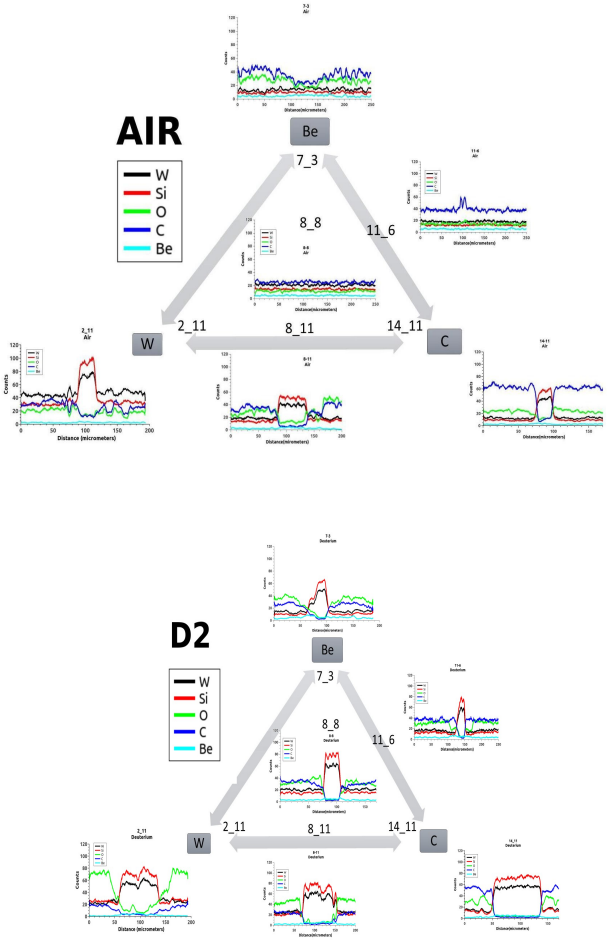


Fig. 5 EDX profiles of the laser irradiated zones a) in air and b) in deuterium

Taking a more closer look at the surface morphology of the irradiated zone peripheries, we can notice that the formed ripples [15-17] period also changes with the ambient gas, respectively is enlarging in the presence of deuterium, as shown in Fig. 6. While for the same irradiated material the ripples size is known to change with the laser incidence angle [18] and fluency [18,19], here none of the above parameters is changing. The only change is in the ambient gas which is also know to influence both through its pressure and composition [20]. The generally accepted mechanism of ripples formation is through the plasmons ('resonant waves') formation during laser-matter interaction [20] mediated by electrons. Thus, the deuterium presence is also affecting the plasmon formation and respectively the ablation process for low power density irradiated zones.

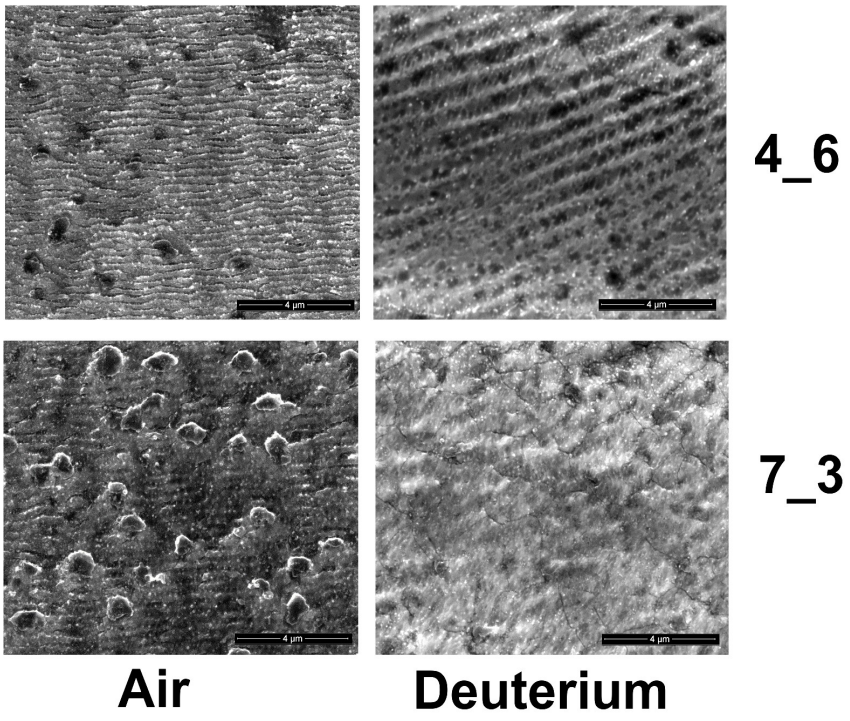


Fig. 6 Comparative ripples images achieved in air and deuterium

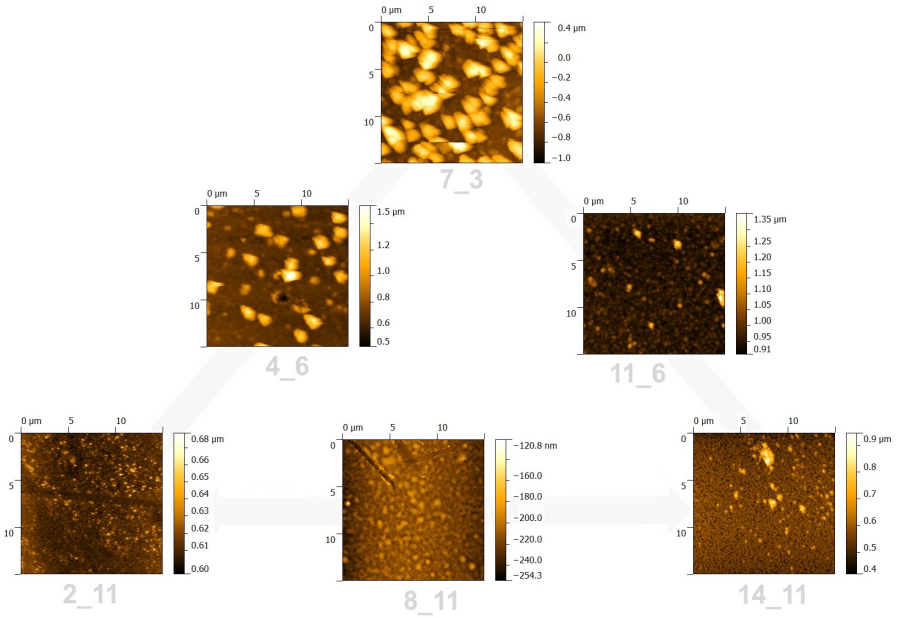


Fig. 7 AFM images of the irradiation zones in deuterium

AFM investigations shows (Fig. 7) an increase of the roughness particularly on Be rich zones, suggesting a possible recrystallization process taking place in Be rich zones.

XPS investigations confirm the W, C and Be elements distributions on the samples and associate the oxygen presence with the Be rich zones, supporting the Be oxidation hypothesis and the BeO composition of the formed structures in the Be rich zones.

Fig. 8 shows the superposed spectra of the analyzed samples, while Fig. 9 shows the percent quantification of the elements presents in the analyzed samples.

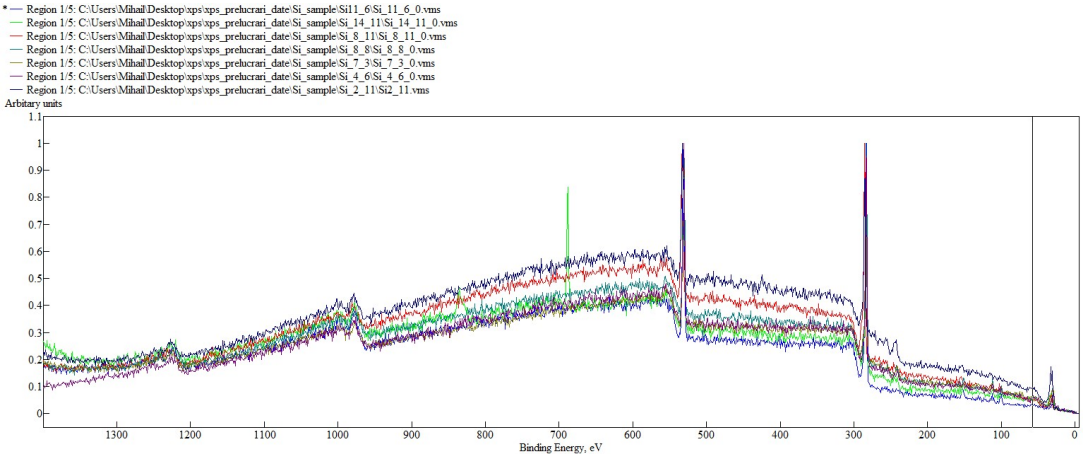


Fig. 8 XPS spectra of the analyzed samples.

Sample code 0-original 1-irradiated	C (%)			O (%)			Be (%)			W (%)		
	O-C=O (289eV)	C-OH (287eV)	C-C, C-H (285 eV)	Bounded oxigen to organic species 531eV	Bounded oxigen to organic species 534eV	Organic oxigen (533eV)	BeC (111eV)	Be metalic	BeO (114eV)	W Metalic (31eV)	WO2 (33eV)	W03 (36eV)
Si2_11	41.1			18.0			39.4			1.5		
	1.7262	4.6443	34.7295	0.612	1.566	15.822	0.617	22.3398	15.8782	0.639	0.519	0.342
Si_4_6_0	42.2			16.1			41.3			0.4		
	2.9118	3.8824	35.448	0.1127	1.4812	14.5061	0.61174	24.367	12.2661	0.1876	0.178	0.0344
Si_4_6_1	44.3			17.9			37.6			0.2		
	2.215	3.8098	38.2752	0.179	1.6468	16.0742	0.6192	21.8456	14.6264	0.0806	0.0808	0.0386
Si_7_3_0	6.1			28.9			64.6			0.4		
	0.2745	0.6039	5.2216	0.289	1.2716	27.3394	0.82145	8.398	47.5456	0.164	0.1792	0.0564
Si_7_3_1	39.9			19.9			39.5			0.6		
	0.6384	2.6733	36.5883	0.0796	0.4776	19.3428	0.18865	27.6895	8.058	0.2322	0.231	0.1362
Si_8_8_0	40.7			17.6			41.1			0.6		
	1.7501	2.5641	36.3451	0.176	1.32	16.104	0.54252	24.9066	13.5219	0.2694	0.2532	0.0774
Si_8_8_1	29.2			17.7			52.6			0.5		
	1.1096	2.482	25.6084	0.1062	0.6549	16.9212	0.34448	29.6664	18.2522	0.2395	0.229	0.031
Si_11_6_0	43.8			16.3			39.7			0.1		
	3.2412	3.9858	36.5292	0.0326	0.1793	16.1044	0.07118	20.0485	17.9841	0.0412	0.045	0.0138
Si_11_6_1	43.2			16.5			40.2			0.1		
	0.2592	4.6656	38.2752	0.0165	1.749	14.718	0.7031	20.8236	18.5322	0.0422	0.0352	0.0226
Si_14_11_0	40.1			15.8			43.5			0.6		
	1.7243	3.8496	34.5261	0.4582	2.0698	13.272	0.90036	25.317	16.269	0.18	0.1932	0.2268
Si_14_11_1	42.2			18.9			38.5			0.5		
	0.422	2.0678	39.7524	0.7938	1.5309	16.5564	0.5894	20.9055	16.2085	0.1535	0.156	0.1905

Fig. 9. Percent quantification of the elements presents in the analyzed samples.

It also suggests a strict correlation between the C percents and the C-C concentrations (Fig. 10) (We exclude the C-OD presence since oxygen and deuterium are not simultaneously in comparable concentrations in the irradiation chamber).

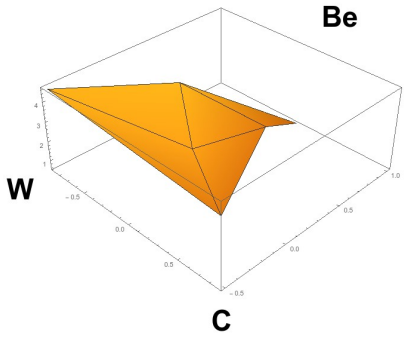


Fig. 10 XPS results: C-C (and and possible C-OH / C-OD) bounds on the laser irradiated zones

FT-IR spectra measured over the laser irradiated zones have several broad signals: a signal around 1040-1060 cm^{-1} assigned to Si-O-Si stretch vibrations and a signal at 1180 cm^{-1} that might appear due Si-O-Si domains. Absorption band at 1100 cm^{-1} could appear due to C-O-C stretching as well. Since in the region 2800-2950 cm^{-1} was not observed increase in C-H stretching and no C-D stretching bonds were observed in region 2100-2200 cm^{-1}, it can be concluded that signals at 1410 and 1500 cm^{-1} correspond to C-C stretches in aromatic ring, probably through laser-induced faze transition processes [21,22] confirming the presence of carbon in graphite-like structures. The signal at 860 cm^{-1} might indicate the presence of Si and/or W oxides

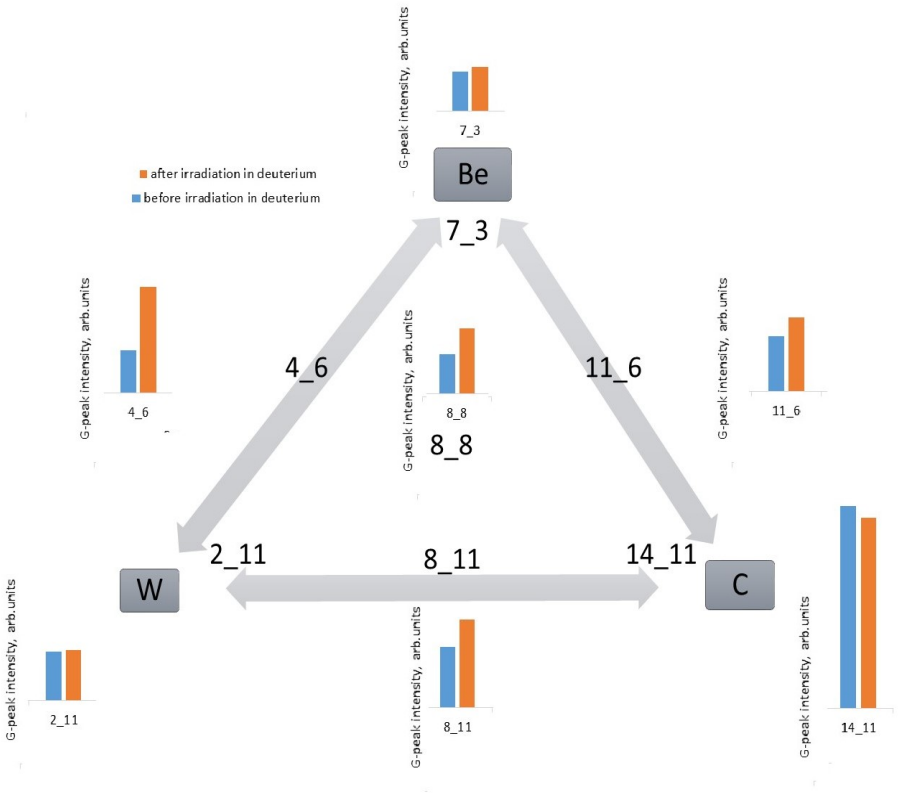


Fig. 11. Comparative G peak intensities in Raman investigation of non-irradiated zones of the samples before and after laser irradiation in deuterium

Deuterium has not been found within the formed bonds with the sample's elements. However, Raman investigations have shown some differences between the samples

before and after being exposed to the deuterium. Raman investigations of the non-exposed zones of the samples were performed and a diagram of the graphite related peak before and after deuterium exposure is presented in Fig. 8 It could be noticed a general tendency of graphite peak increase after the exposure to deuterium.

While deuterium presence, and (particularly ionized deuterium) seems to enhance the graphite G peak intensity, then one possible way is by reducing the presence of the amorphous carbon. Such a reduction could take place by simply reacting with the weakly bounded carbon atoms:

$$2\,D_2 + C = CD_4\uparrow$$

By methane evaporation the percent of the crystalline graphite increase explaining the enhance of the Raman peak and weakening the material structure, and further amplifying the (thermal) ablation processes [23].

4. Conclusions

TVA deposited layers similar with fusion wall materials were irradiated with high power density laser beam in air ambient conditions and in deuterium at 20 Torr, in order to understand the composition and hydrogen isotopes influence on the material degradation. The carbon content was the one increasing the ablation process while the tungsten the decrease the process. Deuterium gas was proving to enhance the ablation process for all investigated samples. Analyzing the non-irradiated surfaces the increase of the graphite peak was suggesting an amorphous carbon removal by deuterium, possible by deuterated methane formation, while the change of the ripples size formed in low power density irradiated zones was suggesting differences in the plasmon formation depending on the ambient gas composition and pressure. Thus, these are the two proposed mechanisms of the Be-C-W (and particularly carbon based) materials ablation enhancement by deuterium presence.

The activities scheduled in the frame of the project were succesfully accomplished. The scientific results were published within 5 presentations to the international conferences, 2 papers published in ISI journals, 1 paper sent to an ISI journal, and registration of one patent to a national authority (OSIM) and an international one (EPO)

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