

## *STUDY OF THE TERNARY SYSTEM FORMATION Be-C-W USING THERMIONIC VACUUM ARC METHOD; INFLUENCE OF OXYGEN ON THE PROCESS*

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### **1. Introduction**

Mixed materials thin film depositions are used in order to obtain structures that they have the same characteristics as the films that are deposited in different fusion reactor's areas. This type of films can be generated under working conditions of the thermonuclear reactors, where some of the walls are made of beryllium tiles, or beryllium coated inconel tiles, and other reactor regions are made of carbon and tungsten [1]. The high energy plasma determines the migration and mixture of these elements in unwanted places.

As it is well known, within the thermonuclear reactor there is the probability that the heat, ion and especially neutron flux damaging the wall by cracks, material sputtering and transport inside the reactor, superficial film erosion, chemical composition change of the walls, etc. [2]. Tritium and deuterium plasma inside the ITER fusion reactor, which will be in operational use by 2018, reaches a temperature higher than 100 million degrees, and stopping the wall material plasma contamination through the above mentioned mechanisms is the main issue of operating it.

The inner wall is one of the main components of ITER and must be designed so that to be able to remove the plasma's caloric flux, to reduce the nuclear effects inside the vacuum chamber and to protect the superconductive coils against overheating and the radiation damage. The generated fusion power is around 1500MW with a medium neutron flux near the wall of  $1\text{MW/m}^2$ . The inner wall must also endure the plasma disruption heat and electromagnetic loads.

The beryllium-tungsten-carbon combination was never tested inside the tokamak, both materials being of high interest for this purpose. Although tungsten is high temperature resistant (melting point:  $3695^{\circ}\text{C}$ ) and has a very high atomic number, it ionizes very easy, so that the tungsten atoms that reach inside the plasma cause a high energy absorption from the deuterium and tritium ions.

Theoretical analysis using simulations were performed regarding sputtering and erosion combined with plasma evaporated particles transport and their later deposition in other parts of the reactor but the obtained results need to be confirmed through several experiments that use

layers containing different tungsten-beryllium-carbon mixtures and their high energy plasma and ion flux interaction behavior is met to determine the most suited for the tokamak parts that interact with the fusion plasma.

## 2. Experimental set-up

The obtained mixed materials films using the deposition method suggested by the research group from NILPRP will be investigated using experimental conditions similar to the ITER operational/ working conditions (high flux ions, electrons and neutrons bombardment, etc).

The Thermionic Vacuum Arc (TVA) method was used to prepare pure and mixed materials layers to be studied as point of view of morphological, structural and fuel retention properties. The evaporation was performed at a temperature lower than the material's melting point and the deposition process may be obtained using neutral atoms from the material's surface, but also by generating metal vapor plasma, the substrate being bombarded with metallic neutrals as well as ions. The plasma generated ions may be accelerated towards the substrate by applying a bias voltage on the substrates [3].

In order to obtain a variable Be-C-We relative concentrations with different oxygen content into the prepared layers, a setup as in Fig.1 was developed. The distance between the anodes was 20cm and the sample holder-anodes distances were around 25 cm, as the particle flux depends on the distance and the incident angle. The two anodes (one made of pure Be rod and another made by a graphite rod surrounded by 1 mm in diameter tungsten wires) and the substrates were positioned so that a different particle flux was present for each sample in a deposition batch.

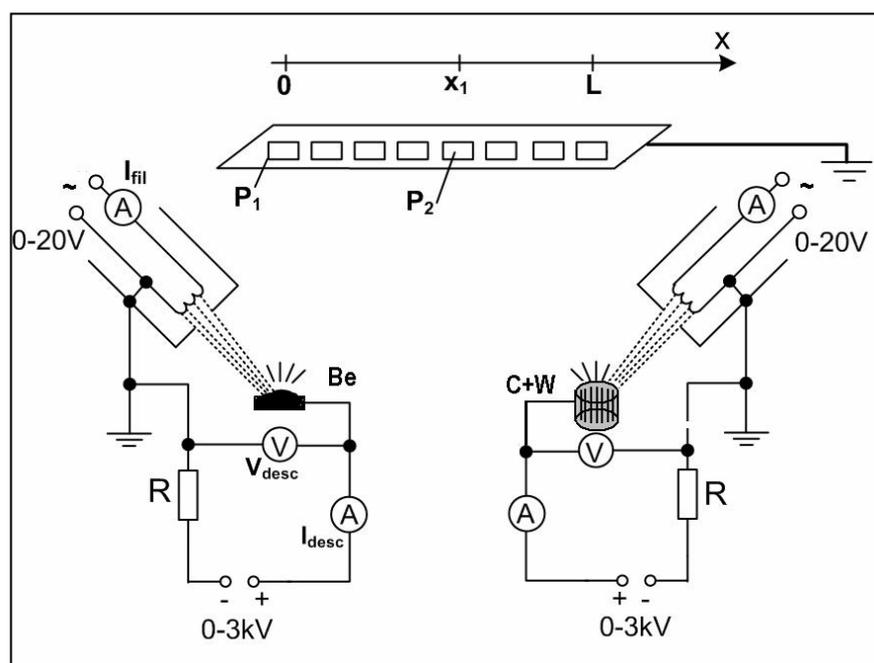


Fig.1. Schematic representation of the deposition system and the electrical connections used to obtain mixed Be-C-W layers.

If several samples are placed at different distances to the two evaporation sources (as shown in figure 1), it is possible to obtain almost continuum concentration variation.

The electron beams evaporate both the Be and the C-W used as anodes, by applying high voltages (1-5kV) between cathodes and respectively anodes. Bright plasmas in pure beryllium and carbon-tungsten atoms are ignited simultaneously. The plasmas are independently controlled by the electron beams (thermo-electrons) emitted by the heated cathodes and the applied voltage on the anodes, in order to obtain the desired concentrations. The oxygen was introduced into the layers adjusting the evaporation rates, allowing the residual gas from the reaction chamber to enter the layers just during their formation. In order to increase the oxygen content, the residual gas pressure was controlled by adding additional oxygen gas. The depositions were performed usually at  $5 \cdot 10^{-6}$  torr, residual air, and at  $5 \cdot 10^{-5}$  torr in residual atmosphere of oxygen.

## **2.1 Substrates and deposition conditions**

For each batch, carbon and silicon substrates were used. The carbon substrates were mirror polished fine grain graphite. The substrates were 12 by 15 mm rectangular shape. In the first two batches, the films were deposited at room temperature, while for the next two, an oven was used to heat them at 350, and 500C respectively. This way, the atoms and the ions from the plasma, reach the substrate without causing thermal shocks and the lack of thermal shocks decreases the possibility of getting defects caused by mechanical stress.

The substrates were placed on a holder that was mounted inside the deposition chamber, and put in thermal contact with the oven.

For a better systematization and to improve further calculus, the samples were given coordinates. Doing so,  $x=0$  on the sample holder is exactly above the beryllium anode. The samples were indexed according to the deposition date and their position relative to the anodes. The sample position, index and substrate type are presented in Tables 1-3. Table 4 presents the TVA processing parameters.

*Table 1. Substrate's positions at room temperature deposition*

Samp.	Si	C	Si	C	Si	C	C	Si	C	C	Si	C	Si
Index	P01	P02	P03	P04	P05	P06	P07	P08	P09	P10	P11	P12	P13
x(cm)	-4.5	-3.5	-3	1	2	3.5	10	11.5	12.5	16.5	18	19.5	22.5

*Table 2. Substrate's positions at 350°C temperature deposition*

Samp.	Si	C	Si	C	Si	C	Si	C	Si	C	Si	C	Si	C
Index	P01	P02	P03	P04	P05	P06	P07	P08	P09	P10	P11	P12	P13	P14
x(cm)	-3.5	-2.5	-1.5	2.5	3.5	8	10.5	12.5	13.5	17.5	20	21.5	23	25

*Table3. Substrate's positions at 500°C temperature deposition*

Sample	Si	C	Si	Si	C	Si	Si	C	Si	Si	Si	Si	Si	Si
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Index	P01	P02	P03	P04	P05	P06	P07	P08	P09	P10	P11	P12	P13	P14
x(cm)	-4.5	-3	-1.5	1.5	2.8	4.5	6.5	8	9.5	13	14.5	17.5	20	21.5

Table 4. The parameters for the depositions performed

Tsubstr °C	$I_{fW}$ (A)	$I_{aW}$ (mA)	$U_{aW}$ (V)	W dep.rate (nm/s)	W thickne ss ( $\mu$ m)	$I_{fBe}$ (A)	$I_{aBe}$ (mA)	$U_{aBe}$ (V)	Be dep. rate (nm/s)	Be thicknes s (nm)	Total thickne ss (nm)
R.T	55	1200	1400	0.02	31	42.5	500	830	0.2-0.6	414	445
350	50	2400	900	0.08	131.7	43	450	1000	0.15	269	400.7
500	57	2800	750	0.08	153	46	550	1000	0.1	250	403

### 3. RBS depth profile analysis

RBS measurements were performed to investigate the films compositions, the position of the oxygen and to see if there is a mixture of the three elements. For this it had been used a  $^4\text{He}$  energy beam of 2.6 MeV. The beams energy value was chosen taking into account the interaction cross section of  $^4\text{He}$  and Be to avoid the non-Rutherford interaction that may cause errors in the data interpretation. The fitting of the experimental data was done using SIMNRA code, developed at IPP Garching. Fig. 2 shows the RBS experimental and SIMNRA code simulated spectra of the Be-C-W film deposited on graphite substrate at room temperature and Fig. 3 shows the elemental concentration depth profile of the same film obtained by processing the RBS spectra.

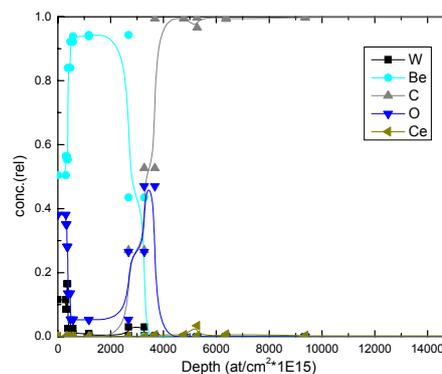
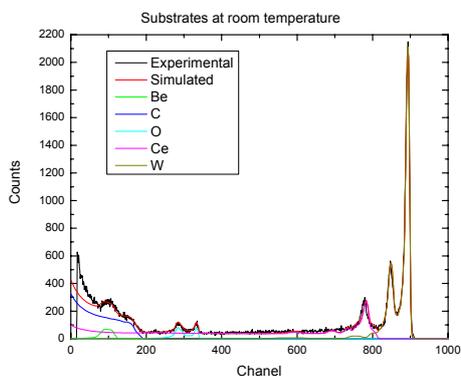


Fig. 2 RBS experimental and SIMNRA code simulated spectra of the Be-W film deposited on graphite substrate at room temperature.

Fig. 3 The depth profile of elemental concentration obtained by processing RBS spectra of the Be-W film deposited on graphite substrate at room temperature.

Fig. 4 shows the RBS experimental and SIMNRA code simulated spectra of the Be-W film deposited on graphite substrate at 500°C and Fig.5 shows the elemental concentration depth profile of the same film obtained by processing the RBS spectra

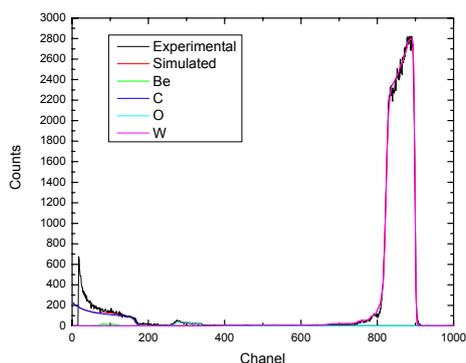


Fig. 4 RBS experimental and SIMNRA code simulated spectra of the Be-W film deposited on graphite substrate at 500°C.

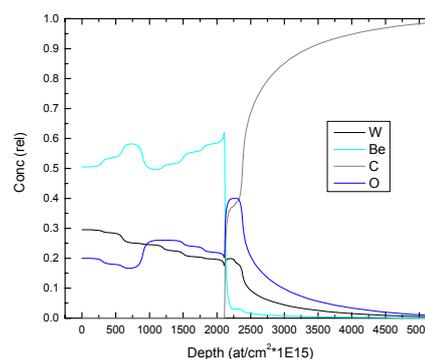


Fig. 5 The depth profile of elemental concentration obtained by processing RBS spectra of the Be-W film deposited on graphite substrate at 500°C

The main aspect underlined by RBS measurements is that for the room temperature substrates the film was oxidized only at the surface and at the interface, while for the heated substrates the oxygen present at the surface, and diffuses into the material, oxidizing the beryllium and the tungsten in the whole film. In addition, the interface oxygen begins to migrate into the substrate as the temperature is increased.

As in RBS method the elements peak shifts with the depth where the material is found in the film, and considering that the thickness of the film cannot be determined with enough precision to know exactly where the interface is, other analysis was needed to check the composition. Although EDS does not give information about the depth profile because it integrates the signal of the distorted electrons, it can give accurate information about the composition. Using the EDS results, we concluded that at the substrate-film interface was identified cerium, material used in graphite substrate polishing.

#### **4. XPS analysis**

The films deposited using two anodes (one Beryllium and the other made of tungsten wires inside a carbon rod) XPS analysis was performed.

For the beryllium inside the film high oxidation occurred. We can argue that this happened during and after the deposition. The ratio also changes as we go inside the film as shown in figures 6 and 7.

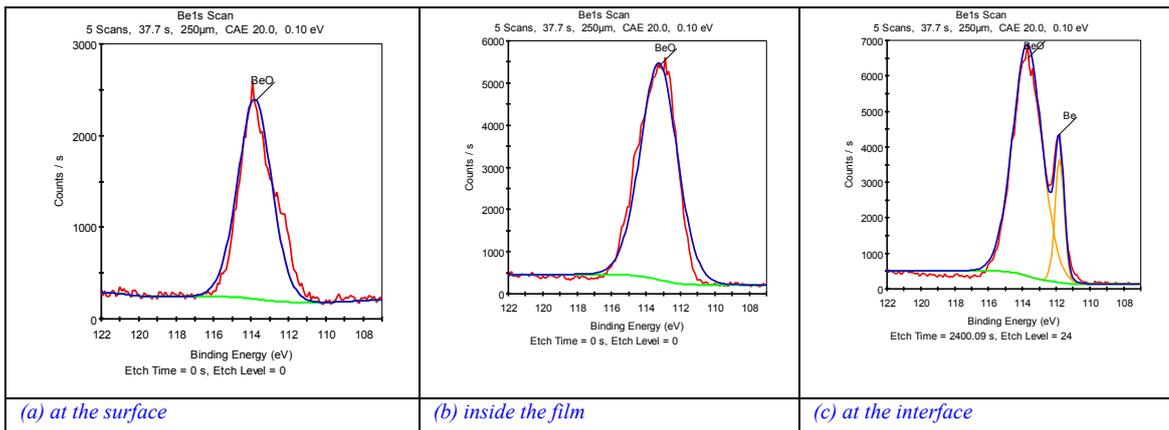


Figure 6. B1s peak at the surface (a), inside the film (b) and at the interface (c)

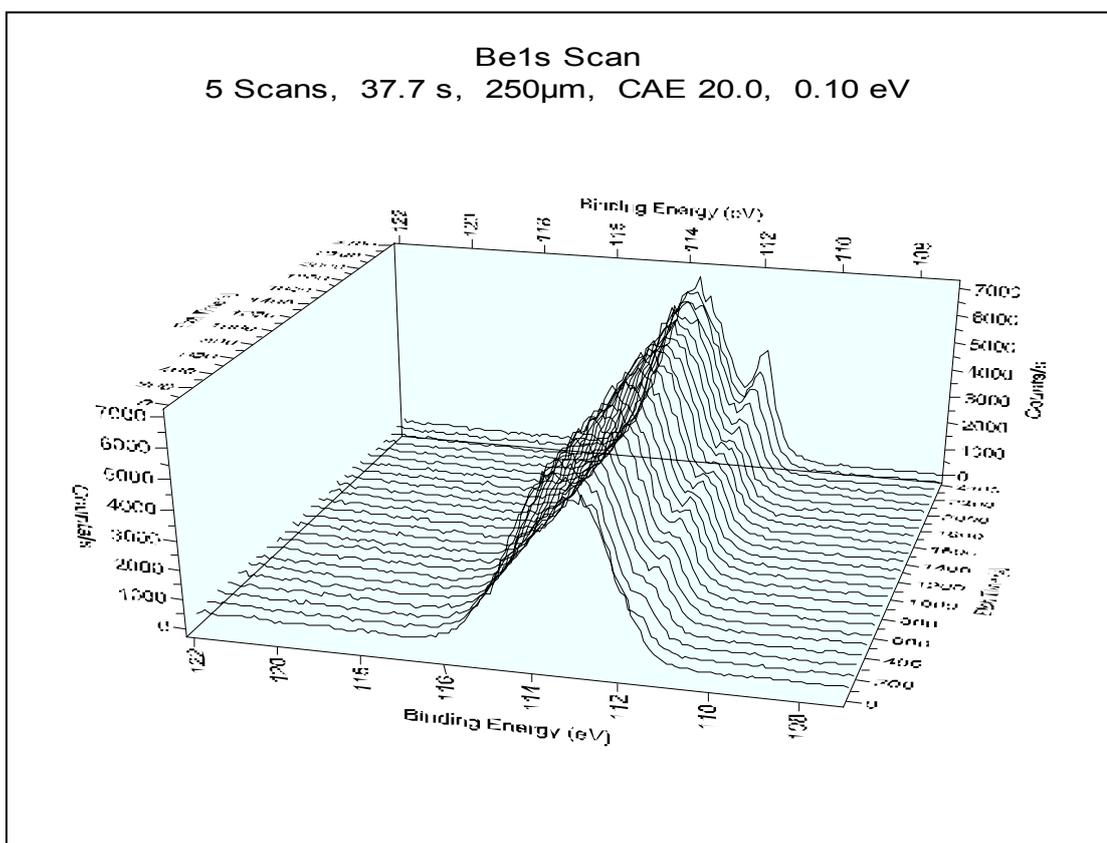


Fig. 7 The depth evolution of the B1s peak.

Fig. 8 shows the evolution of the Be/BeO ratio using the sputtered XPS technique. This way it is proven the fact that the oxidation is higher at the surface and the elemental beryllium is more present inside the film. This fact is shown also in Fig. 9

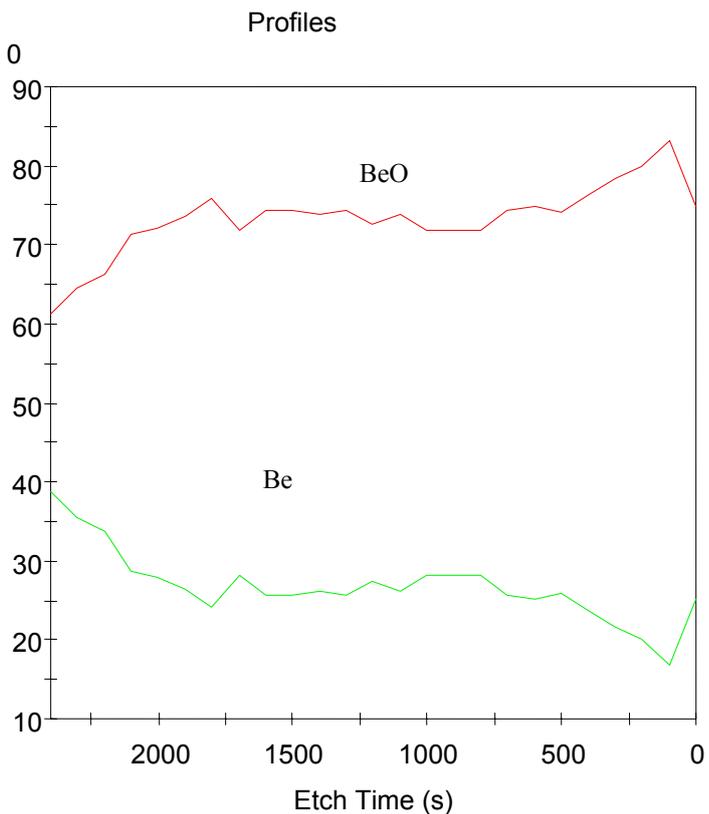


Fig 8 . BeO/Be relative concentrations depth profile

C1s Scan  
 5 Scans, 47.7 s, 250µm, CAE 20.0, 0.10 eV

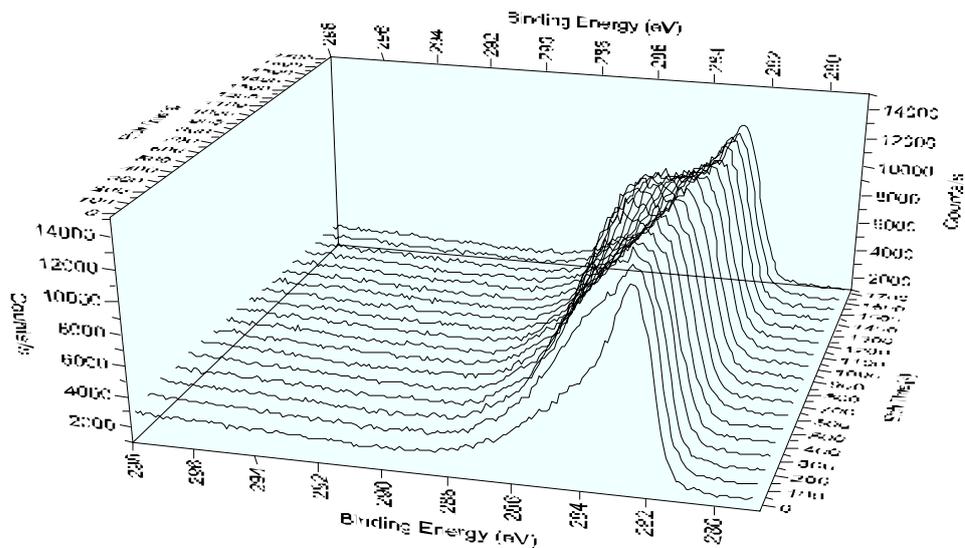


Fig 9 The depth evolution of the C1s peak

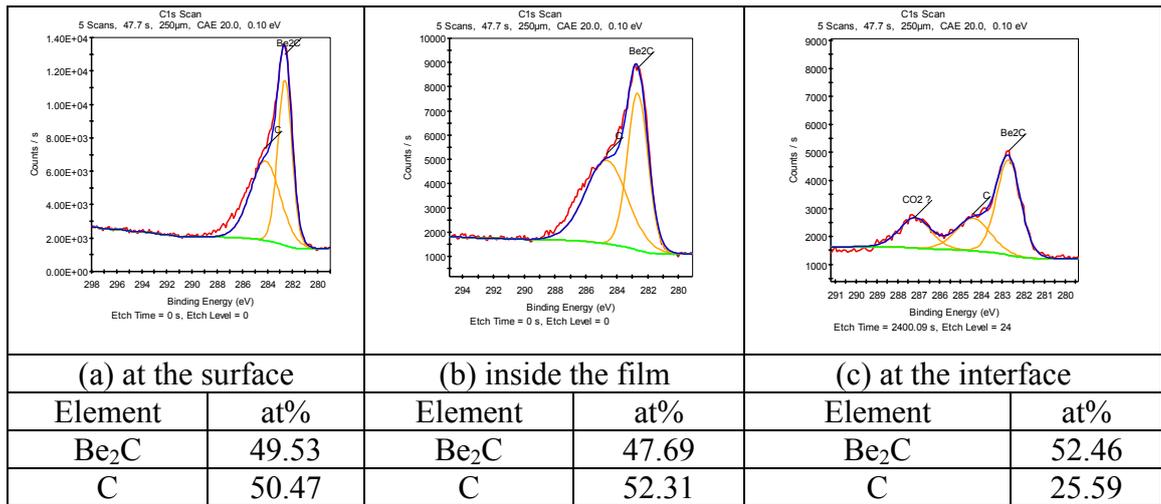


Fig.10 C1s peak at the surface (a), inside the film (b) and at the interface (c) as well as the Be<sub>2</sub>C/C ratios

Carbon C1s peak also changes as with the depth as shown in figure 10. The carbon concentration is very high at the surface but it decreases up to 25 % close to the films interface. For Be-C composite, Fig. 11 that shows for high atomic carbon concentration Be<sub>2</sub>C is present in all the film up to 30%.

Peak to Peak Normalised Height Profile  
5 Scans, 0.25 s, 250µm, CAE 20.0, CAE 20.0

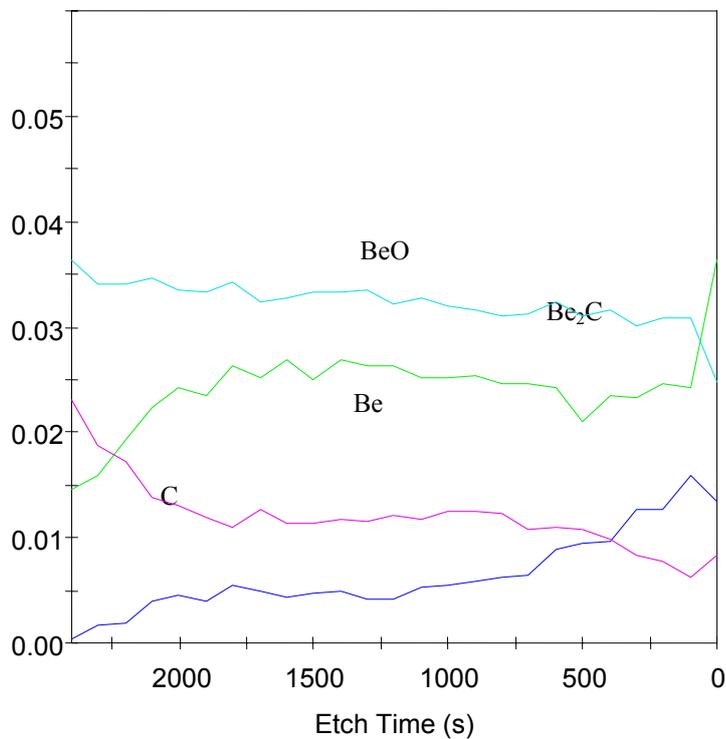


Fig.11 XPS depth profile of a Be-C-W sample deposited at 500°C

The XPS spectrum obtained for the W4f peak at the level “0” (layer not sputtered) is shown in Fig.12, while the same peak after 200 s sputtering (the level 4) is shown in Fig.13.

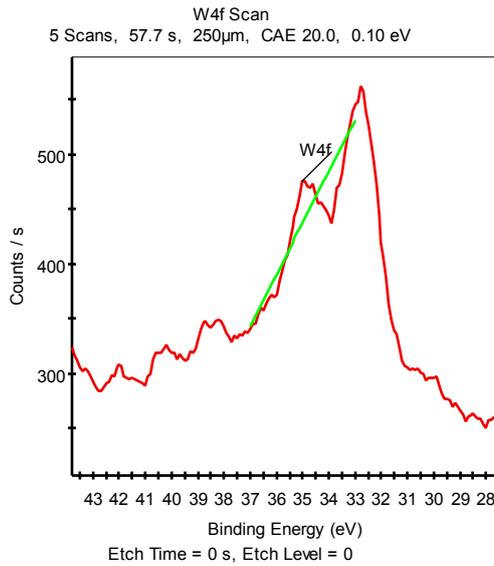


Fig.12 W4f peak, level "0"

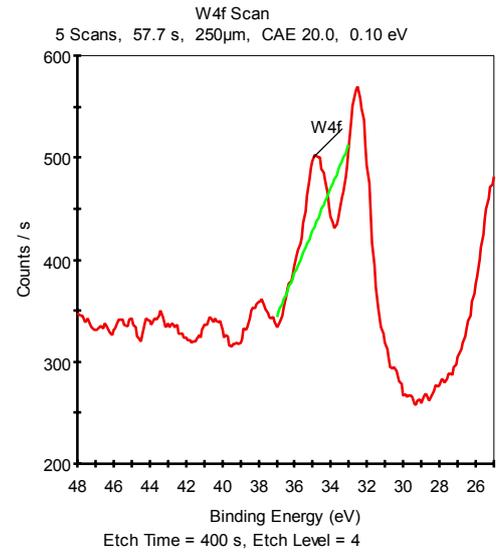


Fig.13 W4f peak, level "4"

3D representation of the XPS W4f peak shown in Fig.14 reveal the W oxidation at the top of the layer and possible formation of the  $Be_xW_y$  chemical compound.

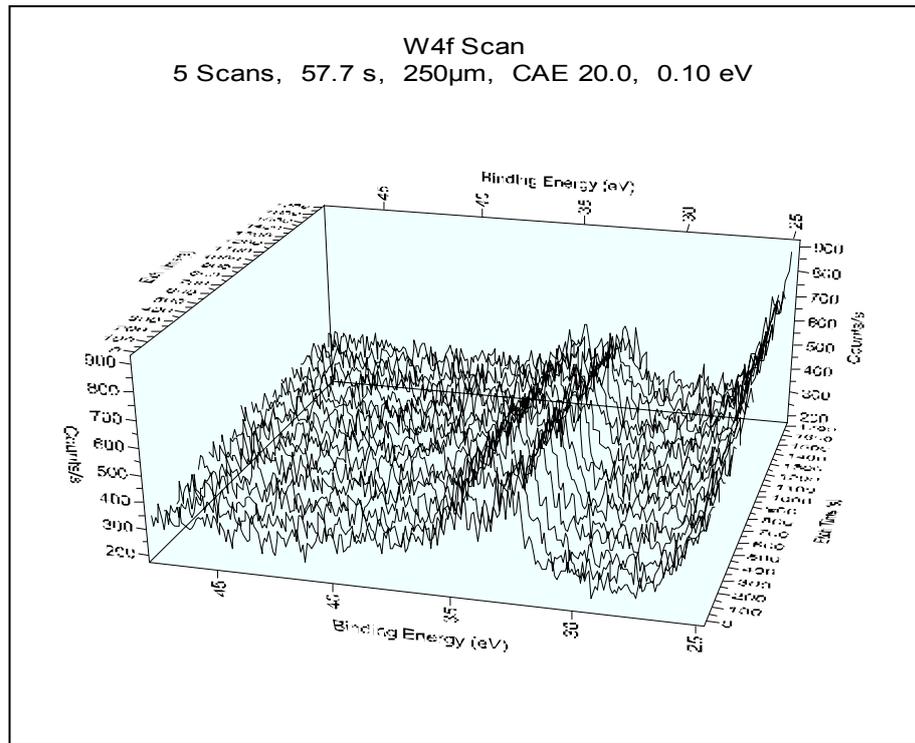
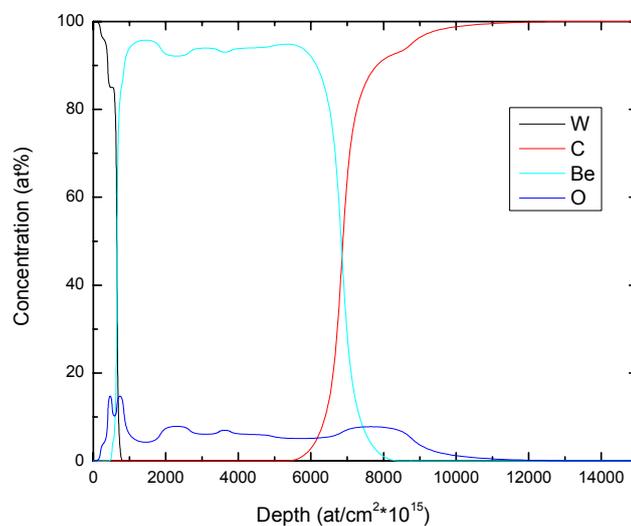


Fig.14. 3D representation of the XPS W4f.

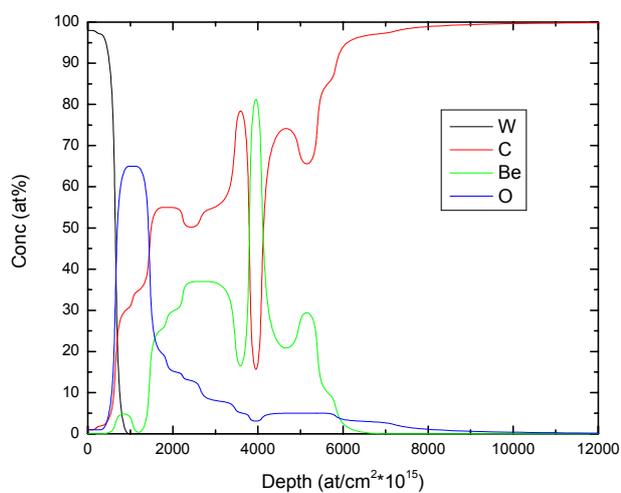
**5. Oxygen migration:**

Fig. 15 presents the RBS depth profile of the 100nmW/200nmBe films coated on the graphite substrate. By the RBS analysis the oxygen concentration is inferred to be higher at the W-Be and Be-C interfaces. After e-beam irradiation using a TVA electron gun, the oxygen concentration from the Be-C interface decreased, and drastically increased at the Be-W

interface. The W layers acts at a barrier of the oxygen present at Be-C interface, as well into the whole deposited film. (Fig.16)



*Fig.15. The depth profile of the 100nmW/200nmBe films coated on the graphite substrate.*



*Fig.16. The depth profile of the 100nmW/200nmBe films coated on the graphite substrate after E-Beam irradiation/annealing at 900°C using a TVA electron gun.*

Analyzing By XPS a 200 nm Be film deposited on graphite substrate, was identified oxygen at the Be-C interface, as shown in Fig.17. After a thermal annealing at 750°C in vacuum, was observed the migration of the BeO compound toward the surface as shown in Fig.18

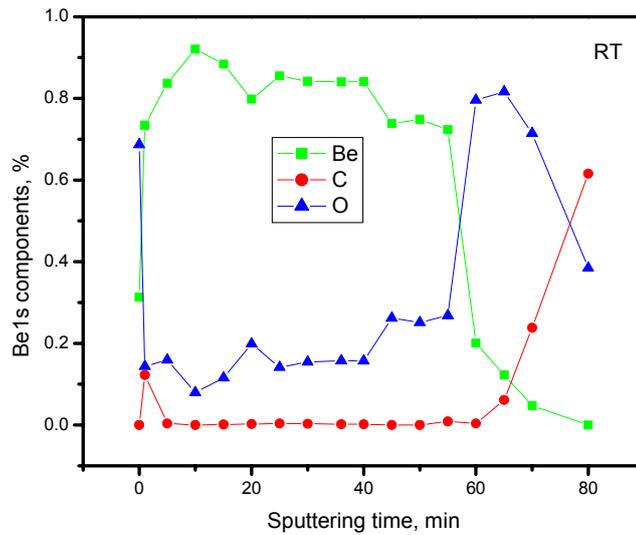


Fig.17. The depth profile of the 200nm Be films coated on the gaphite substrate.

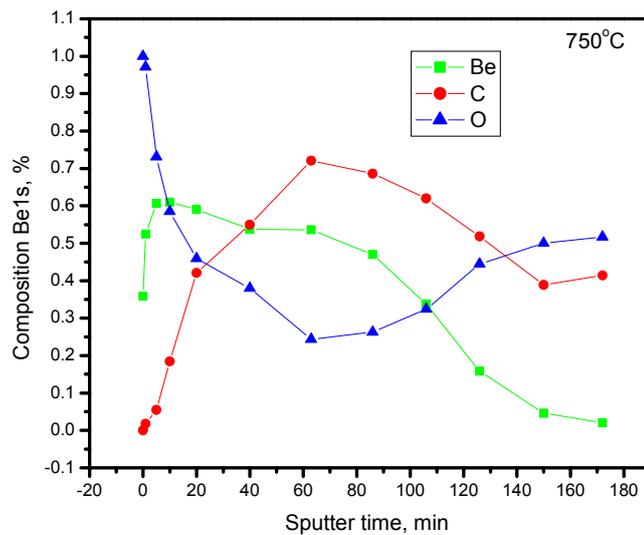


Fig.18. The depth profile of the 200nm Be films coated on the gaphite substrate after annealing at 750°C in vacuum.

Fig. 19 presents the RBS depth profile of the 200nmBe films coated on the gaphite substrate. By the RBS analysis the oxygen concentration was evidentiated the presence of the oxygen gas at Be-C interfaces. After the annealing in vacuum at 750°C, the oxygen concentration from the Be-C interface decreased, and drastically increased at the Be surface.. (Fig.20)

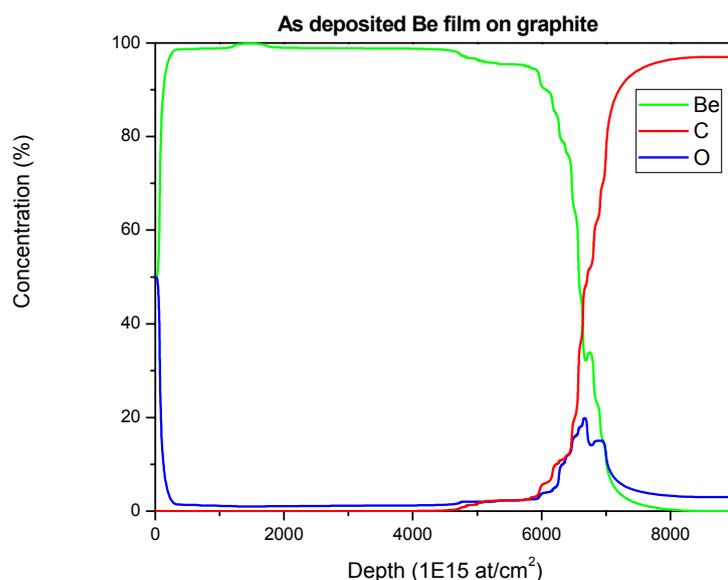


Fig.19. RBS depth profile of the 200nmBe film coated on the graphite substrate.

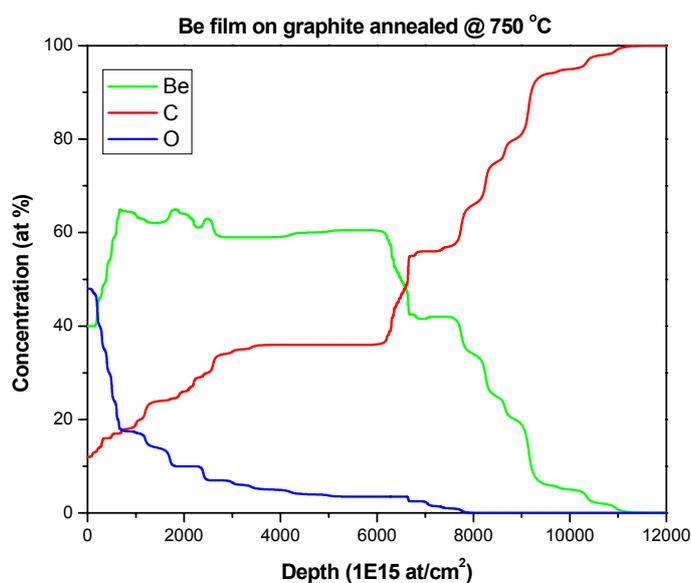


Fig.20. The RBS depth profile of the 200nmBe films coated on the graphite substrate after annealing at 750°C in vacuum.

## 6. SIMS analysis

SIMS (Secondary Ion Mass Spectrometry) analyses were performed at VTT Institute in Helsinki, Finland, using following measurement parameters: VG IX70S double focussing magnetic sector SIMS;  $O_2^+$  (5keV) primary ions, ion current 250nA, sputtered area 300 x 220  $\mu m^2$ ; Sputter rates: 0.56nm/s (Be/W).

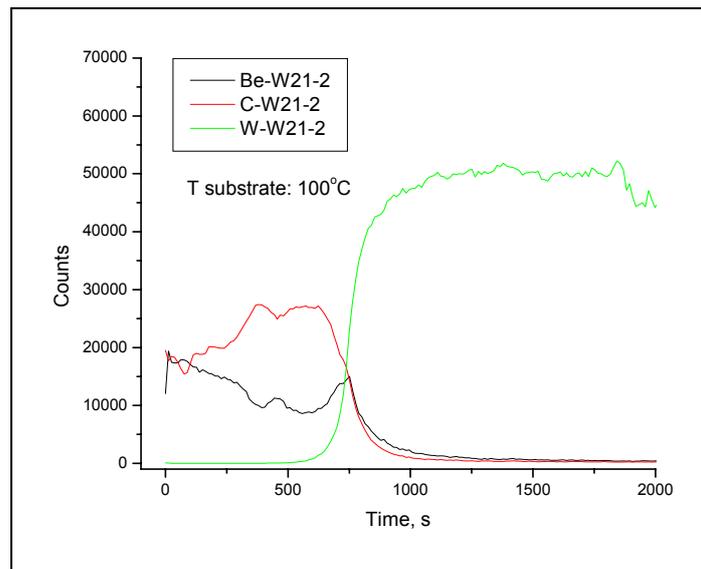


Fig.21 SIMS analysis of a Be-C-W mixed layer deposited at 100°C (equivalent to RT)

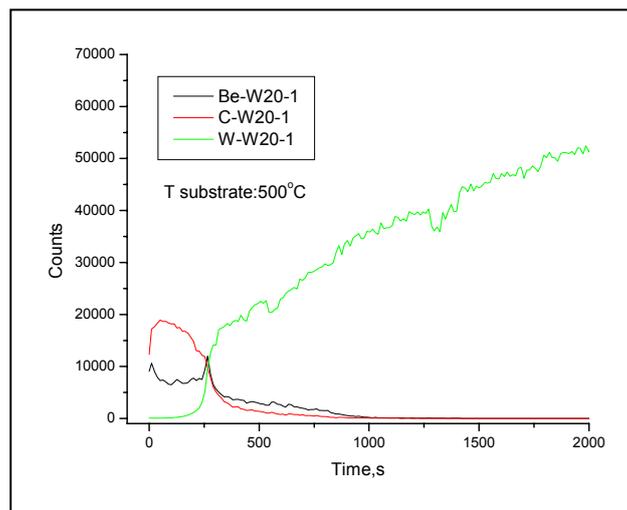


Fig.22 SIMS analysis of a Be-C-W mixed layer deposited at 500°C.

Both Be-C-W samples prepared at 100°C (sample name 20W, deposited at 100°C, equivalent to RT) and 500°C (sample name 21W) were analyzed. The thicknesses of the coatings are: 200nm (20W) and 560nm (21W). Be has a peak at the W/coating and the top of the mixed layer. The interface peak is broader on sample W21 (100°C) than on sample W20 (500°C) which could be due to higher substrate temperature. The interface peaks may indicate a reaction between W and Be.

## **7. Conclusions**

The original Thermionic Vacuum Arc method (TVA) developed by our team, was used for preparation of Be-C-W mixed layers with different oxygen content into the prepared films. The oxygen was introduced into the layers adjusting the evaporation rates, allowing the residual

gas from the reaction chamber to enter the layers just during their formation. The residual gas pressure was controlled by adding additional oxygen gas. The depositions were performed at  $5 \cdot 10^{-6}$  torr, residual air, and at  $5 \cdot 10^{-5}$  torr in residual atmosphere of oxygen.

XPS and SIMS analyses proved the formation of Be/W, BeO compounds at film-substrate interfaces and BeO, CO, compounds at the top of the prepared coatings.

The main aspect underlined by RBS measurements is that for the room temperature substrates the film was oxidized only at the surface and at the interface, while for the heated substrates the oxygen was present at the surface, and diffuses into the material, oxidizing the beryllium and the tungsten in the whole film. In addition, the interface oxygen begins to migrate into the substrate as the temperature increased [4-8].

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