COMPOUND FORMATION IN BINARY MIXING OF Be, C AND W

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1. Introduction

The current design of ITER involves the use of beryllium (Be), carbon fiber composite (CFC) and tungsten (W) as plasma facing materials. It is expected that Be eroded from the first wall and ionized in the *scrape-off-layer* (SOL) plasma will be mainly re-deposited at divertor surfaces leading to the formation of mixed materials films and corresponding changes of the original material properties of W and C. The in-vessel fuel retention inventory is one of the key issues affected by the mixed material systems. Its and the development of control strategies require a detailed knowledge of both retention and release behaviour of such mixed systems.

After the Be/W ratio was determined by MeV ion beam analysis the films were exposed to a deuterium ion beam using the IPP Garching High Current Ion Source. The energy of the D ion beam was 600 eV D_3^+ (i.e. 200 eV/D) with implantation performed at normal incidence to the target surface at different target temperatures (room temperature, 200 ºC and 350 ºC). Deuterium retention was measured also as function of deuterium fluence in the range of 10^{21} to 10^{23} D/m^2 for each sample. After deuterium implantation, the near surface (up to a depth of 1 μm) amount of D retained in the films was determined by Nuclear Reaction Analysis (NRA) using the ^{3}He(D,^{4}He)p reaction. As expected, the retention behavior of the films varies as a function of Be/W ratio from that of a pure Be-like behavior at low W concentration, to that of polycrystalline W-like behaviour at high W concentration.

The deuterium release behavior of the films was investigated by Thermal Desorption Spectrometry using the TESS facility at IPP Garching. It turned out that by increasing the W concentration, the low temperature D_2 release peak characteristic to pure Be (present at ≈ 200 ºC [2]) becomes broader and decreases. The experimental results will be interpreted in terms of the underlying fundamental processes and their effect not only from D fluency and implantation temperature, but also from the morphology and the structure of the films which was determined by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

2. Coatings using TVA method

Tungsten and beryllium multilayers were coated on W, graphite and silicon substrates at substrates temperatures of 100; 300 si 500 ^{O}C. The experiments were carried out in a stainless steel vacuum chamber using thermionic vacuum arc (TVA) method developed at NILRP [1, 2].

The evaporation ensemble consists of a beryllium or tungsten anode and a grounded electron source – the cathode. The electron source is made of a loop filament of W wire externally heated with electrical currents of 60 to 120 A (see Fig. 1).

For metals with low vapour pressure (less than 10^{-1}torr) at their melting temperature, ignition of the TVA plasma can only be obtained if the metal is melted in a crucible. For the other metals with high melting points like tungsten, the anode is a rod which is evaporated from the top, like a candle; no crucible is needed. Tungsten rods are only available as sintered material. As such materials contain high amounts of impurities with different vapour pressures at a certain temperature, unwanted sparks appear and ignition of the TVA plasma is not possible using such an anode. A specially designed anode allowed ignition of very stable plasma in W vapours. The W anode consisted of a bunch of thin W wire (0.2 mm) which allowed thorough melting of the material upon electron heating, as can be seen in Fig. 1.[1]

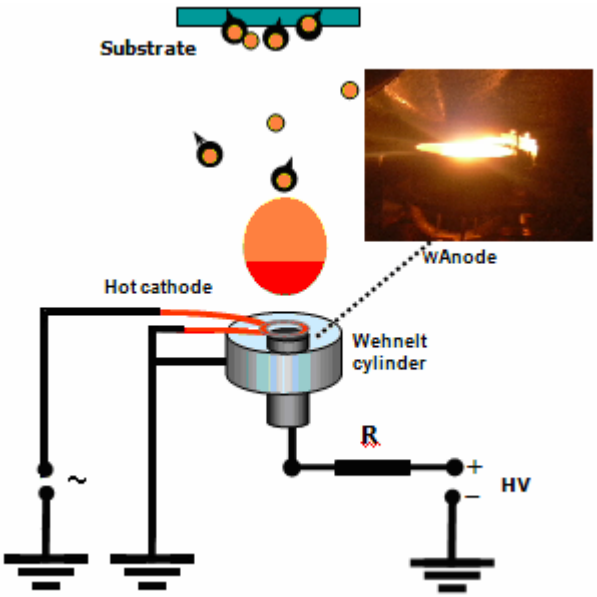


Fig. 1. Experimental setup of Thermionic Vacuum Arc method for W deposition. Inset image: anode made of W wires.

Beryllium was also deposited using a beryllium rod in order to produce pure Be films without impurities that can be generated by the crucible [1]. As the TVA plasma is localized at the anode and does not fill the vacuum chamber, ions and neutrals escape from the plasma and travel without collisions (negligible phenomenon) towards the chamber walls. The ions escape from the plasma due to the potential difference between the plasma and the grounded chamber walls. A bias negative potential was applied on the samples in order to increase the kinetic energy of W or Be ions to produce compact, dense layers.

Were prepared multilayers on W, Si and C (graphite) substrates in the following sequence: Be films of 300-500nm + W films of 20-10nm. Were prepared also mixed layers of

Be-C and Be-W in order to determine the fuel retention, in cooperation with specialists of IPP Garching, Germany.

The process parameters are shown below, as collected form the operating process journal:

Be, W deposition (substrate at 100°C)

Sample arrangement:

Samp.	Si1	C2	Si3		C4	Si 5	C6		C7	Si 8	C9	C10	Si 11	C12	Si 13
Pos (cm)	-4.5	-3.5	-3		1	2	3.5		10	11.5	12.5	16.5	18	19.5	22.5

W Anode Be Anode

Deposition parameters:

$P_{initial} = 8.2*10^{-6}$ torr

For Tungsten: For Beryllium:

$U_{a-W} = 1400V$

$I_{a-W} = 1200mA$

$rata_W = 0,02nm/s$

$I_{f-W} = 55A$

$U_{a-Be} = 830V$

$I_{a-Be} = 500mA$

$rata_{Be} = 0,2nm/s, dar$ initial $0.6nm/s$

$I_{f-Be} = 42.8A$

Substrates temperature reached 260^0 C at the end of the process.

Deposited layer above each anode: Be: 414nm

W: 31nm

Be, W deposition (substrate heated at 300^0 C)

Sample arrangement:

Samp.	Si 1	C 2	Si 3		C 4	Si 5		C 6	Si 7	C 8	Si 9	C 10	Si 11	C 12	Si 13	C 14
Pos (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

W Anode Be Anode

Deposition parameters:

$P_{initial} = 2.3*10^{-5}$ torr

For Tungsten: For Beryllium:

$U_{a-W} = 800 - 900V$ $U_{a-Be} = 1000V$

$I_{a-W} = 2300 - 2500mA$ $I_{a-Be} = 450mA$

$rata_W = 0,08nm/s - \text{constanta}$ $rata_{Be} = 0,15nm/s - \text{constanta}$

$I_{f-W} = 50A$ $I_{f-Be} = 43A$

Substrates temperature reached 310^0C at the end of the process.

Deposited layer above each anode: Be: 269nm

W: 131.7nm

Note: Very shiny samples and color gradient from W to Be

Be-W co-deposition (substrate heated at 500^0C)

Sample arrangement:

Samp.	Si 1	C 2	Si 3		Si 4	C 5	Si 6		Si 7	C 8	Si 9	Si 10	Si 11	Si 12	Si 13	Si 14
Pos (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

W Anode Be Anode

Deposition parameters:

$P_{initial} = 9.5*10^{-6}$ torr

For Tungsten: For Beryllium:

$U_{a-W} = 750V$ $U_{a-Be} = 1000V$

$I_{a-W} = 2800mA$ $I_{a-Be} = 550mA$

$rata_W = 0,08nm/s - \text{constanta}$ $rata_{Be} = 0,1nm/s - \text{constanta}$

$I_{f-W} = 57A$ $I_{f-Be} = 46A$

Substrates temperature reached 360^0C at the end of the process.

Deposited layer above each anode: Be: 250nm

W: 153nm

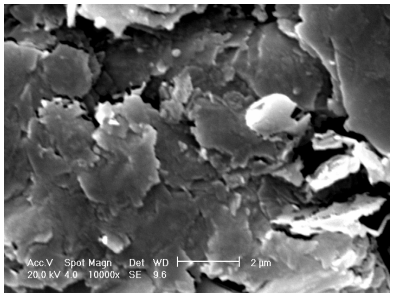
Note: Very shiny samples and color gradient from W to Be

3. SEM analyses

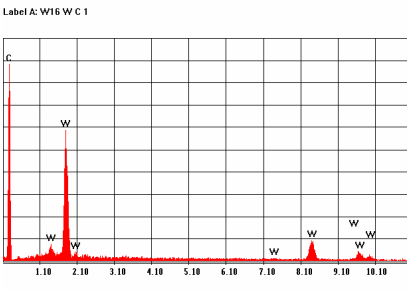
The morphology of the substrates and the deposited films was analyzed using a scanning electron microscope Philips ESEM XL 30 TMP operating at 20-30kV. The scanning electron microscope ESEM has all characteristics of and usual SEM microscope, but it can operate in the low vacuum mode, allowing analysis of nonconductive samples, for example.

The microscope has an EDS (Energy Dispersive Spectrometer) device, able to determine the compositional, qualitative and quantitative distribution of an element, as well the surface elemental mapping of a certain sample.

Were obtained secondary electron images and compositional analyses bulletins.



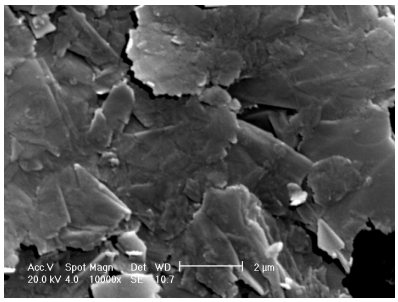
W/C 1



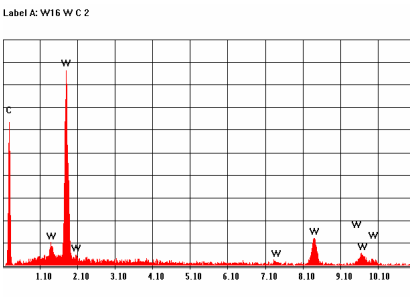
W/C 1

Element	Wt %	At %
C	70.72	97.37
W	29.28	2.63
Total	100.000	100.000

W/C 1



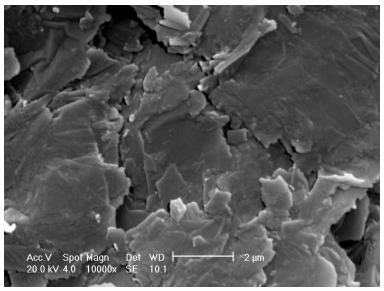
W/C 2



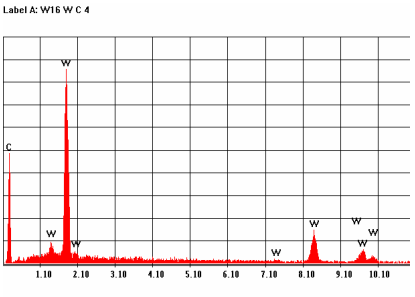
W/C 2

Element	Wt %	At %
C	61.18	96.02
W	38.82	3.98
Total	100.000	100.000

W/C 2



W/C 4



W/C 4

Element	Wt %	At %
C	54.06	94.74
W	45.94	5.26
Total	100.000	100.000

W/C 4

Fig. 2. SEM secondary electron images and compositional analyses bulletins of the W films deposited on C substrates. (W films of 20 nm (W/C 1), 40 nm (W/C 2) and 60 nm (W/C 4)

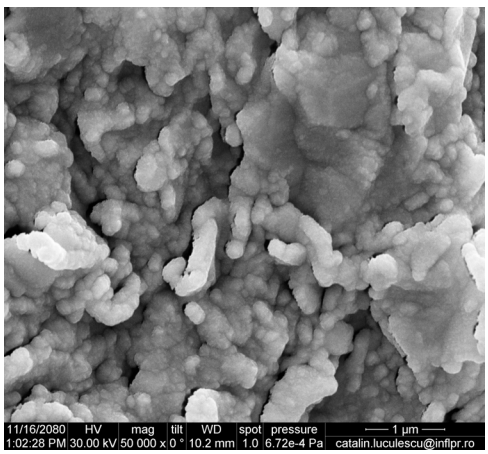


Fig. 3. SEM image of a 300 nm W film coated on C(graphite) substrate

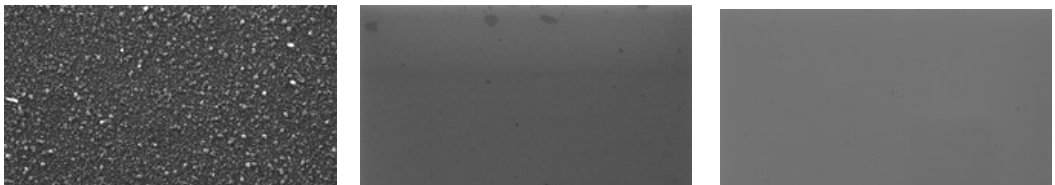


Fig. 4 Be-W at 100°C; Be: 60.55%; O:36.21 %; W:3.25 %

Fig. 5. Be-W at 300°C; Be: 12.52 %; O: 22.98 %; W: 64.48 %

Fig. 6. Be-W at 500°C; Be: 11.83 %, O: 18.09 %; W: 70.06 %

4. AFM analysis

The atomic force microscopy (AFM) data were recorded in non-contact operating mode using a Park XE-100 equipment (silicon tip with conical shape).

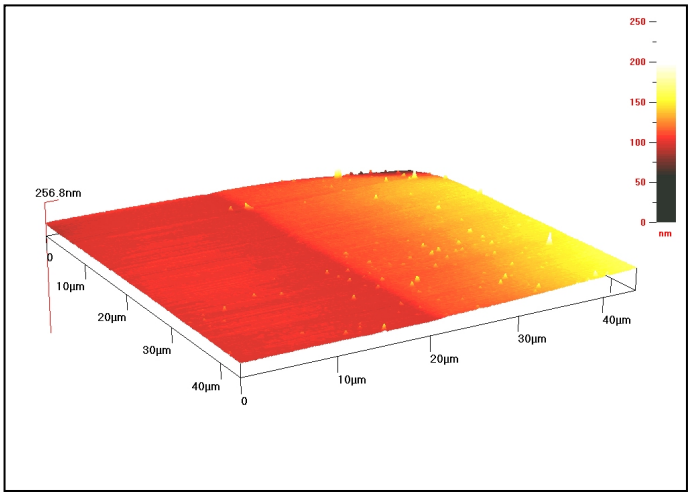


Fig. 7. AFM image of a 100 mm Befilm coated with 50 nm W coated on Si substrate.

We used the horizontally line by line flattening as planarization method. The topographical AFM images in combination with a subsequent statistical data analysis, including the calculation of the root mean square roughness and power spectral density (PSD) analysis gave detailed information about the surface morphology. A typically AFM image of a Be/W film shows a smooth film surface with a step of 100 nm between the coated and uncoated area of a silicon substrate. (Fig.7)

5. 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 μm^2 ; Sputter rates: 0.56nm/s (Be/W): Be/W on silicon samples 17Si, 18Si and 19Si contain carbon, iron, nickel, copper and molybdenium in the W/Be interface.

Sample 19Si has some hydrogen at the Be/Si interface. There is some carbon in the Be/Si interface. Be has a peak in the W/Be interface and this could be due to matrix effects;

secondary ion yield may change at the interface which changes the signal intensity even though the Be amount may be constant. Another possibility is that W and Be react at the interface. Be-oxide signal seems to be more stable than beryllium. BeO/Be signal ratio varies as a function of substrate temperature; it is highest for sample 19Si (100°C) and smallest for 17Si (500°C).

It has to be pointed out that the Be-oxide signal is not real oxide signal because samples were bombarded with oxygen beam and thus oxygen signal is at least partly due to the primary beam. The tail of W signal seems to broaden as a function of the substrate temperature. The long tail in the beryllium and beryllium oxide signals in the silicon substrate can be due to SIMS parameters. Iron (56) and nickel (58) signals in the Si substrate are not real iron and nickel signals; they are due to silicon molecular signals $^{28}Si_2$ and $^{29}Si_2$. Thicknesses of the layers are given in Table 1.Depth profiles of Be/W coatings are presented in Figs. 8-10.

Table 1. Thickness of Be/W samples, as determined by SIMS analysis

Sample	Thickness of W layer (nm)	Thickness of Be layer (nm)
17Si: Be/W at 100°C	65	340
18Si: Be/W at 300°C	58	385
19Si: Be/W at 500°C	64	365

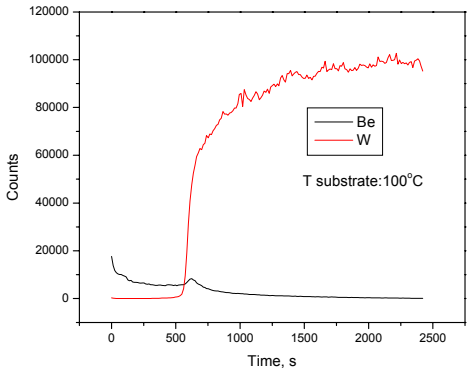


Fig.8 SIMS depth profile of the Be/W sample deposited at 100°C

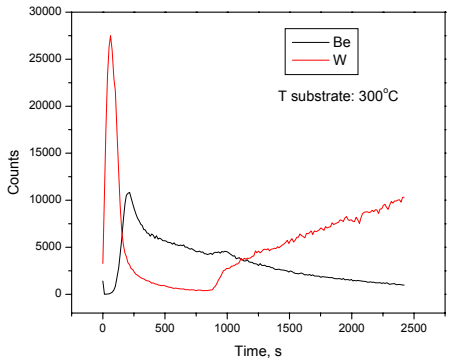


Fig. 9 SIMS depth profile of the Be/W sample deposited at 300°C

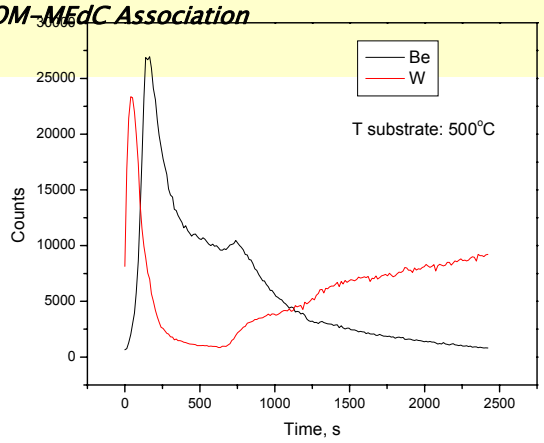


Fig. 10 SIMS depth profile of the Be/W sample deposited at 500°C

6. RBS analysis

From RBS measurements it was revealed that no impurities except oxygen were present in the film. Fig. 11 presents the RBS spectrum obtained using a 2.6 MeV ^{4}He ion beam. From it, one can see that the tungsten is not uniformly distributed into the film; on the top surface of the film the tungsten concentration is lower than near the film substrate interface. Also, the presence of the oxygen at the film-substrate interface and on top surface is observed.

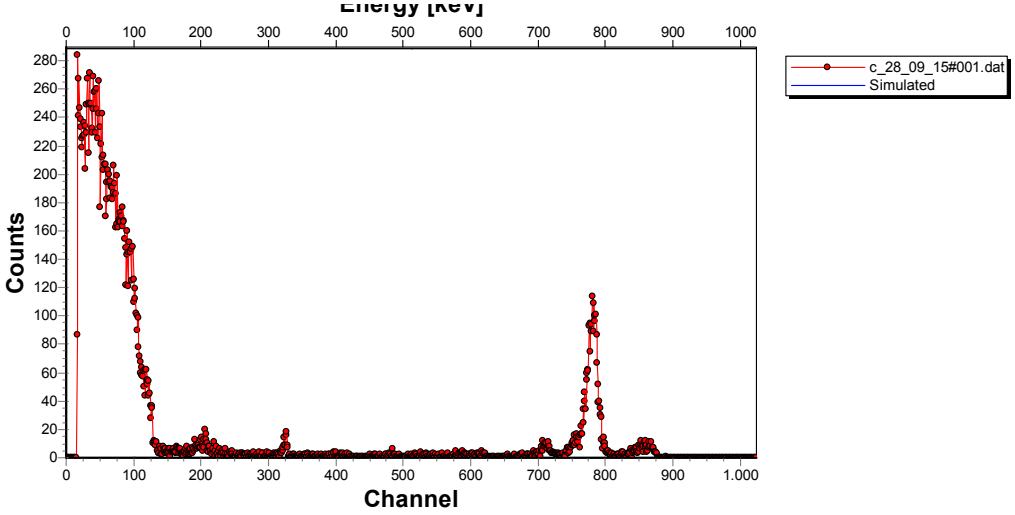


Figure 11. Experimental RBS spectra of a Be-W mixed film deposited on graphite

In order to study the fuel retention in this Be-W mixed films, deuterium implantation was performed at IPP Garching in the High Current Ion Source. The energy of D ion beam was 600 eV D_3^+ (meaning 200 eV/D) at an incident direction normal to the target surface at room temperature. The fluence was 5 x 10^{22} D/m^2 for each sample. After the implantation, the amount of D retained in the films was determined by Nuclear Reaction Analysis (NRA) using ^{3}He ion beam. Thermal Desorption Spectrometry (TDS) was also performed in TESS facility of IPP Garching. The temperature ramp was 15K/min the same as for pure Be films. The TDS measurements revealed the presence of a sharp low temperature desorption peak at ~ 200º C, characteristic to pure Be, where almost all the deuterium is desorbed from the sample. Also, a

broad peak centered around 300º C was observed. According to the literature, this peak, which is characteristic to pure tungsten, can be attributed to the tungsten presence in the film. For exemplification, in Fig.12 and Fig.13, the TDS spectra obtained for pure Be film as well as for Be-W mixed film are presented.

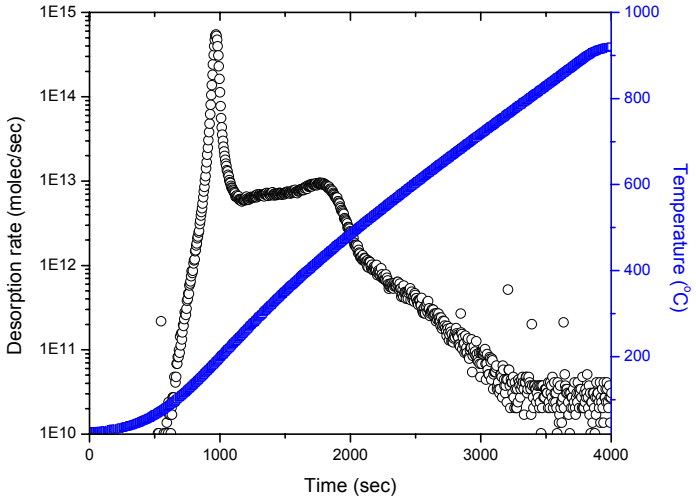


Fig. 11. TDS spectra of a pure Be film deposited on graphite

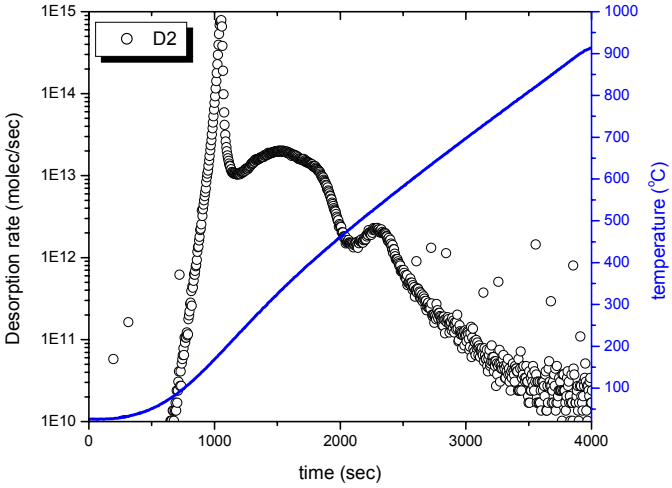


Fig. 12. TDS spectra of a Be-W mixed film deposited on graphite

7. Retention and desorption studies on composite films.

Deuterium implantation was performed in the High Current Ion Source at IPP Garching, Germany. The energy of D ion beam was 600 eV D_3^+ (200 eV/D), and the incident direction was normal to the target surface. The implantation was carried out at a room temperature with the flux of ~ 3 x 10^{19} D/m^{2}s. After certain continuum implantation (1.39 x 10^{22} D/m^2), the amount of D retention was determined by nuclear reaction analysis with using ^{3}He (d, p) α reaction.

The total amount of Deuterium retained as a function of the tungsten concentration is shown in Fig.13.

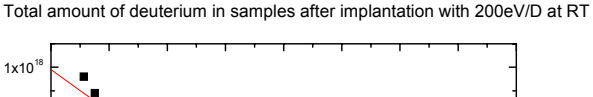


Fig. 13 The total amount of deuterium retained as a function of the tungsten concentration

It is observed that the deuterium retained in the samples depends highly on the Be/W relative concentration. In TESS facility at IPP Garching, thermal desorption spectroscopy (TDS) experiment was performed for the implanted samples. The experiment consists in heating the sample with 15K/min ramp, up to 1000K followed by a 20 minutes hold, and the cooling by it self, measuring the amount of deuterium ejected from the samples. The temperature was measured on the oven, and by having a good calibration previously made (Fig.14), it is possible to correlate the real sample temperature with the deuterium emission.

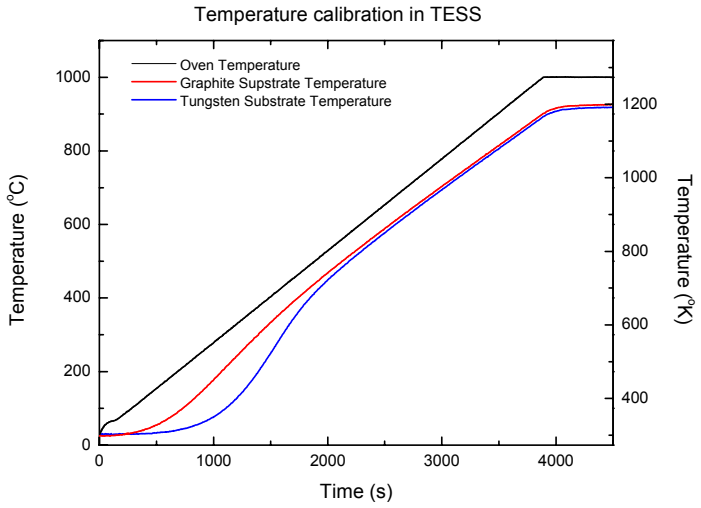


Fig. 14 Substrate temperature calibration in TESS facility

The TDS spectra obtained measuring samples with increased W content are shown in Fig.15. Clearly can be observed the large amount of D2 retained in the samples with low W content.

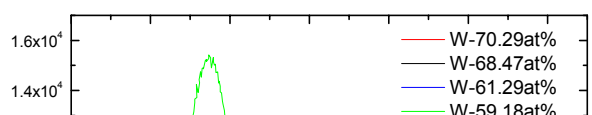


Fig. 15 TDS D_2 spectra of the Be-W films

The Deuterium retained in the samples was measured using NRA method. The results were in good correspondence with the TDS measurements, as shown in Fig. 16. Here is a plot of the amount of deuterium retained inside the sample as a function of the tungsten concentration. As it is shown, the deuterium retained in the sample does have a trend of decreasing with the relative increase of the W concentration.

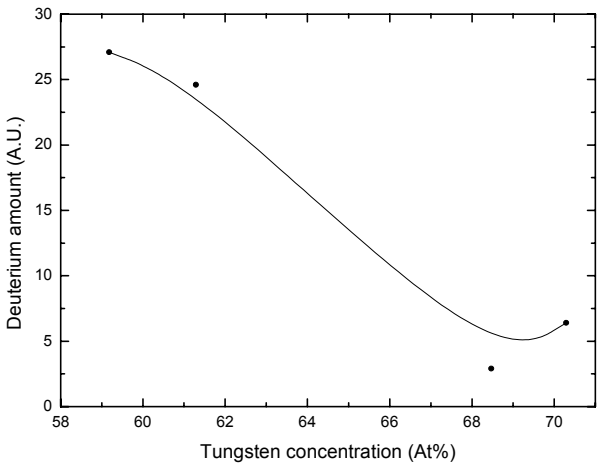


Fig. 16 The deuterium retained in the Be-W samples after TDS

Analyzing the obtained results we can conclude that W presence into the prepared Be/W composite films leads to almost linear decrease of the fuel retention as function of the W concentration [3-6].

8. Conclusions

Were obtained relevant data from the experiments concerning Be, C and W in multilayer as well as binary composite structures prepared using therionic vacuum arc method, at NILPRP.

The influence of the substrate temperature during sample preparation was inffered by SEM, AFM, RBS, NRA and SIMS analyses.

Increased tungsten concentration into the Be-W composite films was found to linerly decrease the fuel retention is such films. The TDS spectra proved that different behavior is caused by different trapping sites for each of these elements.

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