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# Stability of beryllium-carbon coatings under annealing up to 1073 K

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Chemical reactions involving co-deposits in plasma facing components will occur under heat loads. Previous experiments in the Be-C-O system evidenced that compound formation may induce by itself the peel-off of the deposits under annealing in vacuum ( $\sim 5 \times 10^{-6}$  mbar) due to the simultaneous formation of Be<sub>2</sub>C and BeO. When C coatings are deposited on Be plates the two phases growth independently at 973 K in a lamellar structure in the rough topography of C deposits where BeO has space to growth, leading to the huge fracture and peel-off of the films. At higher temperatures similar events occur with the growth of a pure BeO superficial layer. In the reverse case, Be deposited on graphite, the delamination mechanism exist and it is initialise at 973 K. However, it remains scarce. All the experiments point C deposits as a source of dust to the main plasma in operative scenarios when Be is present. Phase formation was followed by X-ray diffraction, ion beam analysis and electron microscopy.

Keywords: carbon, beryllium, phase formation, reverse systems, delamination behaviour

## 1. Introduction

In the restricted group of elements with low neutron activation, beryllium (Be), carbon (C) and tungsten (W) were chosen as the main materials for plasma facing applications [1]. The erosion of the exposed plasma facing components (PFC), and the transport and co-deposition of impurities in other areas of the reactors imposes the formation of mixed materials and compound formation under annealing in the surface of PFCs [2]. Power heat loads will promote the re-emission of the deposited material to the plasma as dust particles. Nevertheless, the same mechanism is enhanced when compound formation induces by itself the peel-off of the deposits, and therefore, it is important to study the chemical and thermal stability of the same materials at elevated temperatures. Compound formation was commonly studied with thin films in the absence of important amounts of oxygen (O). Nevertheless, the gathering of O may be significant as accidental impurity. Be and W tiles will be used in the first wall and divertor of ITER [3]. Nevertheless, earlier designs included W coatings deposited on carbon facing components (graphite based CFC) for the target strike points of ITER divertor [1,3]. Presently, CFC are still in use as support material for W and Be coatings in the Joint European Torus (JET) tiles and the outcomes of the use of CFC in plasma reactors

need to be fully reported. The research at IST involved the investigation of compound formation and stability of the coatings within the Be-C-O and Be-W-O systems. The present document is dedicated to the study of the first one, which was investigated in two reserve conditions, i.e., C and Be coatings deposited on Be and graphite plates, respectively.

Earlier experiments evidenced that the diffusion of Be into C remains weak at 773 K with a diffusion rate of about 65 nm/h [4] (the corresponding diffusion coefficient is of  $2.9 \times 10^{-16}$  cm<sup>2</sup>/s). Nevertheless, the formation of beryllium carbide (Be<sub>2</sub>C) initializes at about 457 K in the Be-C interfaces [5] although it only becomes relevant within the 773 K to 873 K temperature range [5]. Carbide formation may evolve at higher temperatures and depends of the morphology of the films [6]. The chemical stability of beryllium oxide (BeO) is deeply higher than that of Be<sub>2</sub>C, while the standard enthalpy of formation of BeO and Be<sub>2</sub>C are of -609 KJ/mol and -92.5 KJ/mol, respectively [7]. Therefore, and depending of the available O amounts, the growth of the oxide tends to be favored over that of the carbide phase. At a base pressure of about  $5 \times 10^{-6}$  mbar, the formation of BeO is only enhanced at 873 K [6]. Once pure Be, graphite, BeO and Be<sub>2</sub>C have distinct microstructures and thermal expansion coefficients, fracture and delamination in Be-C co-

deposits may occur under thermal stress [6,8,9]. Fractures are commonly enhanced in covalent bond and hard materials such as Be<sub>2</sub>C, or in ionic compounds like BeO which are stable and inert but also hard [8].

In a previous experiment, thin C coatings were evaporated on Be plates and annealed in vacuum in the temperature range from 373 to 1073 K [6]. The only modification observed up to 773 K was the buckling of the C coatings occurred at low temperatures due to the low stiffness of the films. At the same time the Be-C interdiffusion at the interface and the gathering of O at the surface remained very low. At 873 K a reaction front reaches the edge of the buckling structures, where the addition of O is higher than that of the flat zones of the coatings. Possibly, BeO needs free space to growth due to the larger volume of the unit cell of BeO relatively to that of pure Be and it finds the additional space in the rough zones. At 973 K the reaction zone became spread out over the entire blisters surfaces, where the growth of the Be<sub>2</sub>C and BeO components is carried out along parallel lamellas via a discontinuous precipitation process. Be<sub>2</sub>C was found homogeneously distributed over the entire coating's surface, while most of BeO remains restricted to the buckles. The hardness and distinct thermal expansion coefficients of Be<sub>2</sub>C and BeO led to the fracture and final peel-off of the

buckles [6]. Results of this experiment are resumed at the end of section 3 for a better discussion of the new data.

The fracture and the adhesion of Be-C coatings to the substrates depend of the depth profiles and mixing of the formed compounds. As a result, distinct delamination behaviour may occur in the Be-C reverse condition, i.e., when Be coatings are deposited on graphite plates.

## 2. Experiment

For the present experiment, Be coatings were deposited on polished graphite plates by using the thermionic vacuum arc (TVA) method [10]. The coatings were annealed in vacuum with a base pressure close to  $5 \times 10^{-6}$  mbar in the temperature range from 573 to 1073 K by using temperature steps of 100 K and annealing periods of 90 min. Before and after the annealing procedure X-ray diffraction (XRD) spectra were collected for phase identification making use of a Cu X-ray source and a grazing geometry. The X-ray diffraction patterns were identified from the ICDD database [11]. XRD patterns of light compounds as BeO or Be<sub>2</sub>C are difficult to achieve due to the predominant incoherent scattering induced by light atoms [12] and minimum contents of BeO or Be<sub>2</sub>C are necessary for phase identification. In opposition, ion beam analysis (IBA) as

Rutherford backscattering spectrometry (RBS) is particularly useful to quantify Be in thin Be-C-O samples because the individual elemental depth profiles are easily followed by observing the corresponding backscattering yields. In order to follow simultaneously the chemical reactivity of the layers by XRD and by IBA, the Be coatings were deposited on graphite with a nominal thickness of 150 nm. RBS was the used IBA technique and involving 2.0 MeV  $^4\text{He}^+$  incident ion beams. IBA quantifications were performed with the NDF code [13].

Scanning electron microscopy (SEM) involving both secondary (SE) and backscattered electron (BSE) imaging as well as energy-dispersive X-ray spectroscopy (EDX) was carried out for topographic inspection and local chemical analysis. Typically, it is impossible to detect Be by EDX. Nevertheless, C and O amounts are possible to quantify, leading to an evaluation for the formation of BeO at the surface and for C diffusivity (through the Be coatings) towards the surface at different temperatures. The INCA package software was used for EDX quantifications [14].

Structural and mechanical properties of the materials involved in the present work are summarised in Table 1 [15,16] in order to discuss the stability of the coatings.

### 3. Results and discussion

Fig. 1(a) presents the RBS spectra collected from Be coatings deposited on graphite. The energies signalling the presence of Be, C and O on the top of the superficial layers are identified in Fig. 1(a) by vertical arrows. Due to the natural porosity of graphite plates, the Be films are not completely flat and a small amount of C is already visible on the top of the as-deposited sample, where the presence of Be at the surface is also evidenced by the recoil of the C backscattering yield in the as-deposited coating, meaning that almost C is positioned in a deeper depth at the substrate. O is also present at the surface and at the C-Be interface in the same sample. The annealing campaign did not induce significant changes in the elemental depth profiles up to 673 K and at 773 K it is observed just a smooth decrease of the Be backscattering yield with a corresponding advance of the C yield towards the surface, revealing a weak intermixing between C and Be. The advance of the C yield, the C-Be mixing and the O content at the surface are extremely enhanced at higher temperatures, and from 973 K to 1073 K it is also observed a recoil of the C yield, which means that the presence of C on the surface is replaced at 1073 K by a new component. The simultaneous enhancement of the O yield suggests the growth of superficial BeO, as it

was confirmed afterwards by XRD.

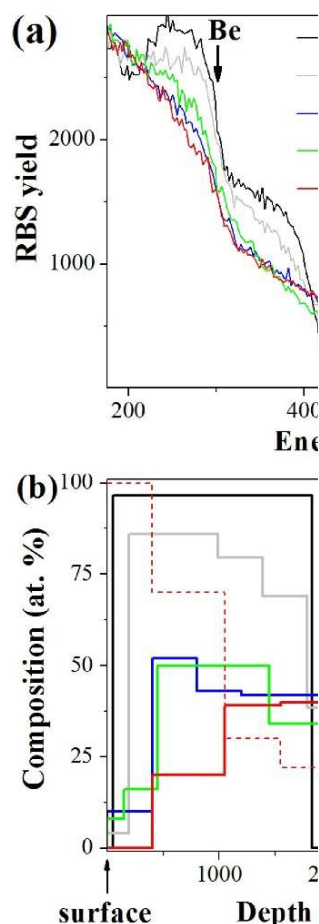


Fig. 1. RBS spectra (2.0 MeV  $^4\text{He}^+$  beams) of Be coatings deposited on graphite before and after annealing (a) and corresponding Be and BeO depth profiles (b) (colours online).

In face of the low enthalpy of formation of BeO relatively to that one of  $\text{Be}_2\text{C}$  and assuming that O reacts preferentially with Be, it is possible to evaluate a content for molecular BeO at the surface from the RBS data. Therefore, Fig. 1(b) presents the results for the depth profile of BeO at 1073 K and for the remaining Be contents during the annealing campaign. At higher temperatures the results are compatible with a preferential

growth of BeO at the surface and with the formation of  $\text{Be}_2\text{C}$  at deeper depths. The composition of the films is completed by the C contents (not represented in Fig 1).

From the diffractograms of the as-deposited and annealed samples (Fig. 2) we observe the formation of  $\text{Be}_2\text{C}$  from 873 to 1073 K, as identified by the characteristic diffraction line of plane (111) at  $35.8^\circ$ . The BeO pattern is also identified from 973 to 1073 K with the peak lines at  $38.5^\circ$  and  $41.2^\circ$  corresponding to planes (100) and (002). All the new RBS and XRD data are in agreement with the ones obtained from the reverse depositions, C deposited on Be plates, while the C-Be mixing and the growth of the carbide and oxide phases occurs at the same temperatures [6]. In particular, the formation of  $\text{Be}_2\text{C}$  is also in agreement with the available data for the diffusivity of C on Be.

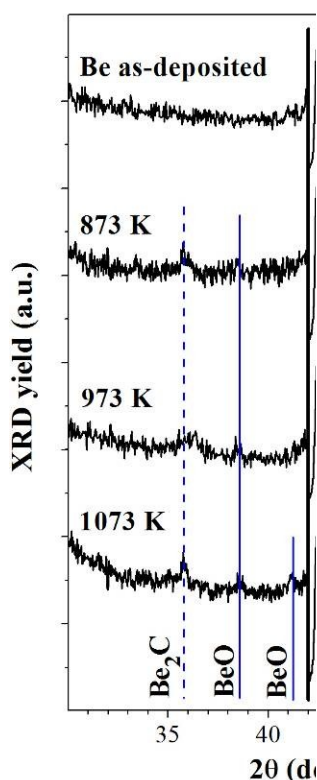


Fig. 2. XRD diffractograms of Be coatings deposited on graphite plates before and after annealing.

In opposition with the buckling mechanism observed in the reverse depositions (C coatings deposited on Be plates) and resumed at the end of section 1, the present annealing campaign did not promote the deformation of the Be coatings, which is explained by the high Young's modulus and stiffness of metallic Be, and also of  $\text{Be}_2\text{C}$  or  $\text{BeO}$  (see the corresponding values in Table 1). Therefore, the addition of O with the formation of  $\text{BeO}$  arises homogeneously distributed along the surface at higher temperatures, while  $\text{Be}_2\text{C}$  remains typically distributed at deeper depths along an extended C-Be interface (see Fig. 3 at 973 K). The segregation between the two phases mitigates the

propagation of (cross-section) cracks under thermal stress within the coating's depth. Nevertheless, materials with high Young's modulus are hard and  $\text{Be}_2\text{C}$  seems too brittle to prevent a very low but partial delamination of the coatings along the interface under thermal stress at 973 and 1073 K, due to the distinct lattice structures and thermal expansion coefficients of  $\text{Be}_2\text{C}$  relatively to graphite (Table 1). Fig. 3(a) shows a SE tilted image of one of the few fracture events observed after annealing at 973 K. A top view of a delaminated area in the same coating and the corresponding EDS elemental maps for O and C are also presented in Fig. 3(b), 4(c) and 4(d), respectively. The EDS results agree with the RBS data, while O is homogeneously distributed in the superficial layer and scarce at the substrate-coating interface as observed in the EDX mapping for O in Fig. 3(c), and C is quite restricted to the graphite substrate in the delaminated area as observed in the EDX mapping for C in Fig. 3(d), revealing, once again, that the oxide and carbide phases grow preferentially at different depths.

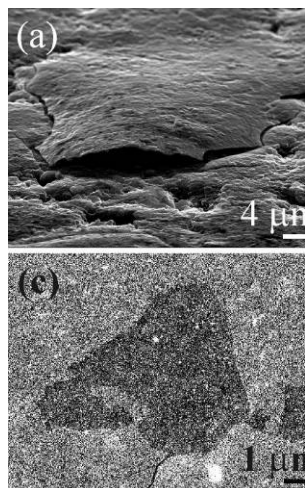


Fig. 3. SE tilted images of a fracture event (a) and top view of a delaminated area at 973 K (d); corresponding EDS maps for the  $\text{K}\alpha_1$  emissions of O (c) and C (d).

The occurrence of delamination events in Be coatings deposited on graphite after annealing revealed to be scarce. Typically,  $\text{BeO}$  is easily formed at the superficial layers and  $\text{Be}_2\text{C}$  is present along an a C-Be interface. The behaviour is completely distinct from that one observed in the reverse conditions, C films deposited on Be plates, where a severe peel-off mechanism occurs at 973 K. In this case, Be needs to diffuse through the C layer towards the surface to oxidise and a significant mixing between the  $\text{BeO}$  and  $\text{Be}_2\text{C}$  phases occurs. The segregation of the two phases with different thermal and structural properties in a lamellar structure enhances the delamination mechanism. In order to evidence the two distinct behaviours, additional SEM images with corresponding EDX elemental maps are presented at the end of section 3 for the reverse system after annealing at 973 K.

Table 1  
Crystalline structure, lattice parameters, Young's modulus and linear thermal expansion coefficients ( $\alpha$ ) of the Be-C-O phases [10,11<sup>\*</sup>].

Phase	space group	a/b/c (pm)	G
graphite	194 (hex.)	246/428/671	6
Be	194 (hex.)	229/-/358	24
$\text{Be}_2\text{C}$	225 (cubic)	433/-/-	31
$\text{BeO}$	186 (trig.)	270/-/439	3

The present work proves that compound formation in the Be-C-O system induces a delamination mechanism under thermal stress, although the behaviour becomes mitigated when Be is deposited on CFCs. Nevertheless, C deposits in tokamaks present irregular and porous morphologies promoting a mixing with other impurities [17] and therefore the emission of significant amounts of dust is expected to occur in a Be-C environment.

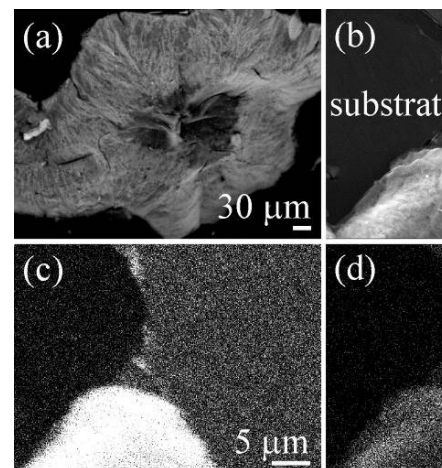


Fig. 4. C coating on Be under 973 K: BSE image of a blister/lamellar structure with  $\text{Be}_2\text{C}$  and  $\text{BeO}$  (a), SE image of a peel-off event (b) and related EDS maps for O (c) and C (d).

#### 4. Conclusions

CFCs are still in use in fusion devices and



they may be a logic choice for some particular applications. The present investigation points the use of CFCs or of any C accidental impurity as an important source of dust emission to the main plasma in presence of Be, while compound formation in the Be-C-O induce by itself the fracture and delamination of co-deposits from PFC. Earlier experiments with C coatings deposited on Be plates plus annealing evidenced a huge fracture and peel-off of the films after annealing at 973 K due to the simultaneous formation of hard BeO and Be<sub>2</sub>C disposed in a lamellar structure along blisters induced by the low stiffness of the C films. In the reverse case with Be coatings deposited on graphite, BeO forms in the surface of the flat films, and Be<sub>2</sub>C grows mainly in an expanded C-Be interface. As a result, the oxide and carbide phases remain quit segregate, mitigating issues caused by thermal stress. Typically, C deposits in tokamaks present irregular morphologies, enhancing the Be<sub>2</sub>C and BeO mixing in Be-C environments. Also the adhesion of Be-C coatings will decrease under power heat loads, leading C or CFC materials as a natural source for dust emission in Be-C environments.

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