The impact of thermal fatigue and carbidisation on the W coatings deposited on CFC tiles for the ITER-like Wall project at JET

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Since August 2011 JET operates with the ITER-like wall comprising bulk Be tiles, bulk W tiles and W coated CFC tiles with a thickness of 10-15 μm and 20-25 μm. In order to evaluate behavior of the W coatings to a cyclic thermal loading relevant to JET operation, High Heat Flux (HHF) tests have been carried out up to 5,100 pulses with an electron beam facility at peak temperatures of 1000°C, 1250°C and 1450°C. The pulse duration was 24 s. Optical inspections of the W layer performed periodically by interrupting the test revealed small delaminations with the size of 50-500 μm. The dependence of the delamination percentage on the number of pulses can be seen as a degradation curve for each particular W coating. In this way the thermo-mechanical properties of the W coatings can be characterized quantitatively. Thermal fatigue and carbidization of the tungsten due to the diffusion of the carbon from the substrate have been recognized as mechanisms for degradation of the coatings. Tungsten carbides have been identified by using TEM (Transmission Electron Microscopy) diffraction analysis on FIB (Focused Ion Beam) prepared cross-section samples subjected to HHF tests. Nano-pores developed at the CFC-Mo and Mo-W interfaces during the tests might be also responsible for the degradation of the coating.

Keywords: Tungsten coating, Carbon fibre composite (CFC), ITER-like wall, High Heat Flux tests, Carbidization

1. Introduction

The extensive research carried out in the R&D phase of the ITER-like Wall (ILW) project at JET demonstrated superior thermo-mechanical properties of the W coatings with Mo interlayer deposited by Combined Magnetron Sputtering and Ion Implantation (CMSII) method in comparison with other PVD or CVD techniques [1]. CMSII technology was used for coating of about 1800 CFC tiles with W layers of 10-15 μm and 20-25 μm for the new ILW of JET [2,3]. Due to the time constraints of the ILW project, only limited tests have been carried out on these coatings. In accordance with the technical specification thermo-mechanical properties were investigated in the hydrogen beam test facility GLADIS at IPP Garching at the following parameters: (i) thermal screening from 6 MW/m^2 – 6 s up to 23 MW/m^2 – 1.5 s (26 pulses in total with a maximum temperature of ~2100°C) and (ii) cycling thermal fatigue at 10.5 MW/m^2 – 5 s – 200 pulses with a peak temperature of about 1500°C. The coatings survived these tests without delaminations. The limits of the coatings which depend on the peak temperature and cyclic time (pulse duration x number of pulses) were not reached. It is very important for the exploitation of the new JET wall to know in advance the limits of the W coatings when they are subjected to a high number of heating pulses (thousands) relevant to JET operation. During normal operation of the tokamak the first wall is subjected simultaneously to long pulse thermal loading (about ten seconds) and high power short pulses (~ 1 ms) produced by ELMs. The objective of the present work was to investigate behavior of the W coatings deposited on CFC substrate by CMSII technology to a large number (> 3000) of long duration pulses. The research was focused on two aspects: (i) quantitative investigation of the delamination depending on the peak temperature and number of pulses and (ii) micro/nano scale investigation of the effects produced by high temperature cyclic thermal loading on the structure and integrity of the W coatings.

2. Experimental setup

Tungsten coated samples were heated by an electron beam and cooled down below the ductile to brittle transition temperature using the High Temperature Test Facility equipment at MEdC-Romanian Euratom Association. The maximum power of the electron beam is 1.5 kW for an accelerating voltage of 15 kV. The cross section of the electron beam on the surface of the testing sample is an ellipse with axes 18/12 mm and an area of ~ 170 mm^2. The electron gun, the diagnostics and the support for the sample to be tested are installed on the top lid of the vacuum chamber (Φ540 x 640 mm). Five Dunlop DMS 780 CFC samples (No.1, 2…5) (30x30x6 mm) have been tested. The nominal thickness of the W coating was 10 μm for two samples and 20 μm for the other three samples. A Mo interlayer of 2-3 μm was introduced to improve the adhesion between W and CFC substrate. The testing sample is installed on a water cooled Cu support (30x30x25 mm) which is positioned by means of the cooling pipes on the axis of the chamber. A special spring system holds the testing

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sample on the water cooled support. A fine graphite powder layer ensures a good thermal contact between the W coated CFC sample and Cu support. This is essential during the experiments because the CFC sample should be cooled down to 200°C as fast as possible after the electron beam was switched off. The water flow rate was ~ 3 l/min. At 3 mm below surface a C type thermocouple (TC) (W5%Re/W26%Re) with a length of 150 mm and a diameter of 1.5 mm was inserted till the middle of the W coated sample. A set of five stainless steel shields were used to protect the thermocouple connector from the heat coming from the sample. The electron beam is coming from the top lid along the chamber axis. The surface temperature is monitored in the range 600-2000 °C by an IMPAC IGA-5 pyrometer which is sensitive in the wavelength range 1.45…1.8 μm. For lower temperatures the pyrometer does not give correct values. The temperature was measured approximately in the middle of the W coated sample. The emissivity of the W coatings was set to 0.5. This was calculated starting from the value of 0.63 measured for W coatings at 1,064 nm.

3. Testing parameters

The testing temperatures and the corresponding power densities are shown in Table 1, where d is the real W coating thickness, A is the delaminated area at the end of test and PD_{estim} is the power density on the W coating estimated by using a calorimetric method.

Table 1 Testing temperatures and power densities

No.	d (μm)	T_{peak} (pyrom.) (°C)	T_{peak} (TC) (°C)	A (mm^2)	PD_{estim} (MW/ m^2)
1	10.9±0.5	1250±50	1050±50	0.34	6.9±0.4
2	10.9±0.5	1450±50	1250±50	3.07	8.4±0.4
3	20.3±0.5	1000±50	900±50	0	4.2±0.2
4	20.3±0.5	1250±50	1050±50	1.70	6.9±0.4
5	20.3±0.5	1450±50	1250±50	10.3	8.4±0.4

For all tests the pulse duration was 24 s. This was the rise time from minimum to peak temperature. The interpulse duration was 35-45 s. The minimum temperature of the sample during the thermal cycling was adjusted by modifying the interpulse duration. More than 3,100 pulses were applied in each test.

4. Experimental results and discussion

The thermal cycling was stopped from time to time and the W coating was inspected with a calibrated stereomicroscope with a magnification from 10 to 45. The objective of these inspections was to count the number of the delaminated zones and to estimate their areas. The maximum number of delaminated zones was 50 cm^{-2} for sample 5. The percentage of the delaminated area was calculated by dividing the total estimated damaged area to the electron beam spot area (~170 mm^2). The graph showing the increase of the damaged area of the W coatings as a result of the thermal cycling tests can be seen in Fig. 1. This kind of curves can be used for quantitative characterization of the thermo-mechanical properties of the coatings deposited on carbon based materials. The thinner coatings have a better behavior from the thermo-mechanical point of view than thicker ones. This might be associated with the heat transfer from the coating surface to the substrate and with the internal stress, which generally increases with the increase of the coating thickness.

The sample No.3 coated with 20 μm of W survived 5,100 pulses at a peak temperature of 1,000 °C without delaminations.

Two SEM (Scanning Electron Microscopy) images of the W coatings in delaminated area are shown in Fig. 2. The delaminations appear as buckling with the size in the range 50-500 μm. Sometimes the coating is detached from the CFC and remains under a certain angle with the surface. By loosing the contact with the substrate these small chips become much hotter than the coating during the electron pulse and sometimes are melted. Locally, in the vicinity of these very hot spots the temperature of the W coating could exceed significantly that measured by pyrometer.

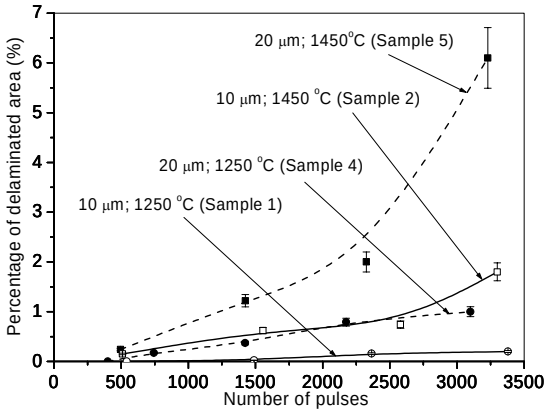
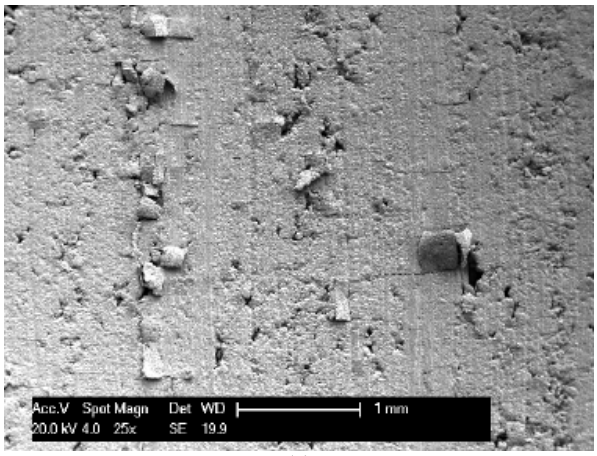


Fig.1 Degradation curves of the W coatings as a result of thermal cycling at 1,250±50°C and 1,450±50°C

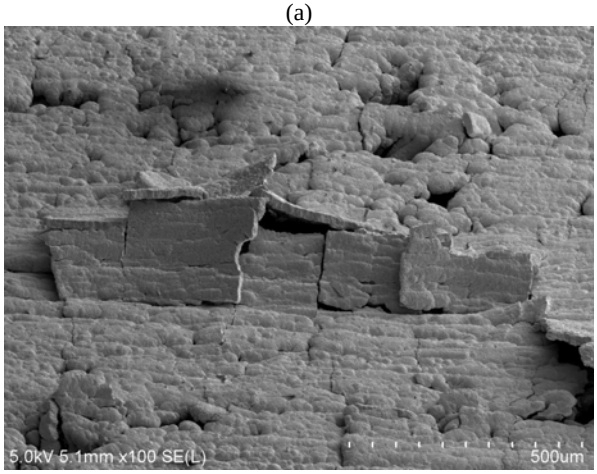
On the small areas where the coating was removed from the surface the electron beam deposits more energy than on W coating since the beam current on CFC is almost twice higher than on W coating. On the other hand the emissivity of those areas is significant higher that that of W coating, so the radiated energy is higher. Consequently, their temperature does not increase. The only hot spots which have been seen during the electron beam heating corresponded to the delaminations as those shown in Fig.2.

Analyses carried out by EDX (Energy Dispersive X-Ray) in the delaminated area indicated the presence of Mo, C and some traces of W (Fig.3). It appears that the Mo-W interface was affected during the thermal cycling. In order to investigate this aspect SEM analyses have been carried out on the non-damaged zones at different distances from a delaminated area using FIB cutting technique. At 10 mm (Fig.4) one can clearly see chains of nano/micro-pores formed at both Mo-C and Mo-W interfaces. TEM analyses demonstrated that the Mo interlayer was transformed into molybdenum carbide and above this layer tungsten carbides started to be formed. It is important to notice that in the right side of the picture, where the Mo-W interface was much more affected the

WC layer is thinner. Similar carbides layers were detected at 5 mm from the delamination.



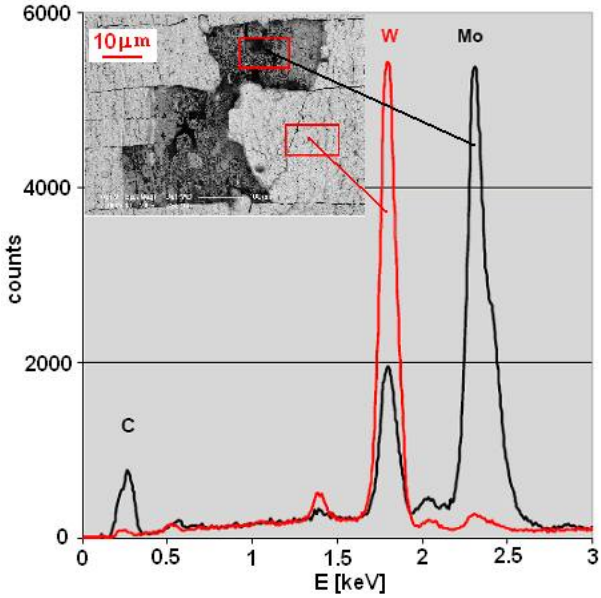
(a)



(b)

Fig.2 General view of the sample No.4 (a) and detailed view of the delaminations on the W coating No.5 after thermal cycling at 3200 pulses (b)

At 0.2 mm away from the delaminated zone no W carbides have been detected by TEM. As it can be seen in Fig. 5 the interfaces and the Mo interlayer were severely damaged in that area. This was probably caused by a higher temperature of the coating produced near the delaminated chip that was melted and re-solidified many times. The structure of that chip contains many pores with dimensions of 10-1000 nm as it can be seen in Fig. 6. This might be associated with the difference of thermal expansion coefficients of these materials, but not only because at melting temperature pores in the micron range are formed into the whole volume of the W coating. The density and dimensions of the pores depend on the temperature and on the cyclic time. Initially, before starting the HHF test, the interfaces are in good condition, without pores, as it can be seen in Fig.7. If the surface temperature on a region of interest during the HHF test is moderate (~ 1200°C) the diffusion of carbon from the substrate and formation of carbides occur simultaneously with the formation of nano-pores at the CFC-Mo and Mo-W interfaces. These nano-pores, due to their small dimensions, reduce the diffusion coefficient of carbon, buy they do not stop the diffusion process. After a certain time of testing, a thin carbide layer will be formed above the Mo-W interface (Fig.4).



(a)

Fig.3 SEM image and the EDX analysis of the composition for delaminated and non-delaminated areas on the sample No.5

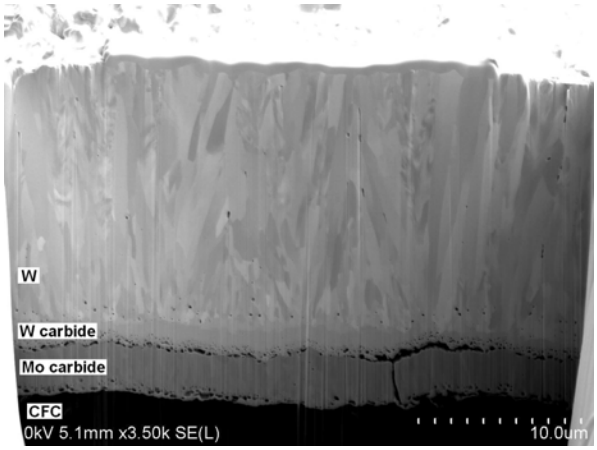


Fig.4. SEM image of a cross section through the sample No.5 taken at the end of test in a non-delaminated zone at 10 mm away of a delaminated chip

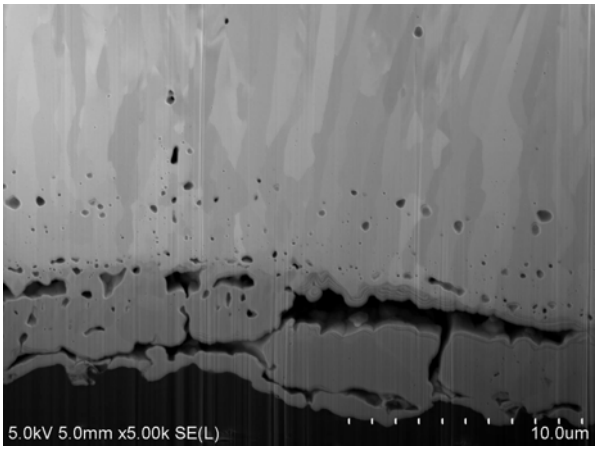


Fig. 5 SEM image of a cross section through the sample No.5 taken at the end of test in a non-delaminated zone at 0.2 mm away of a delaminated chip

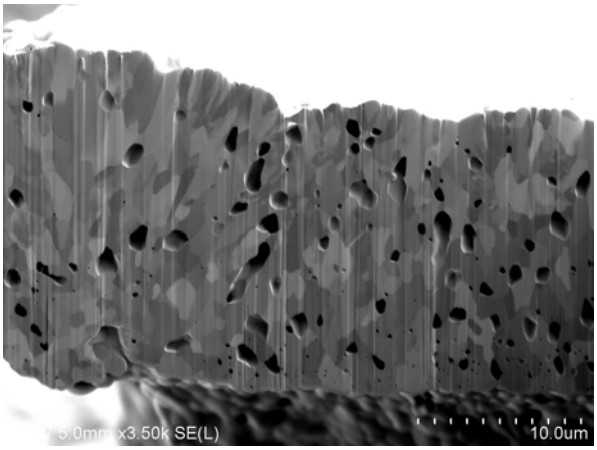


Fig. 6 SEM image of a cross section through a delaminated chip melted and re-solidified many times

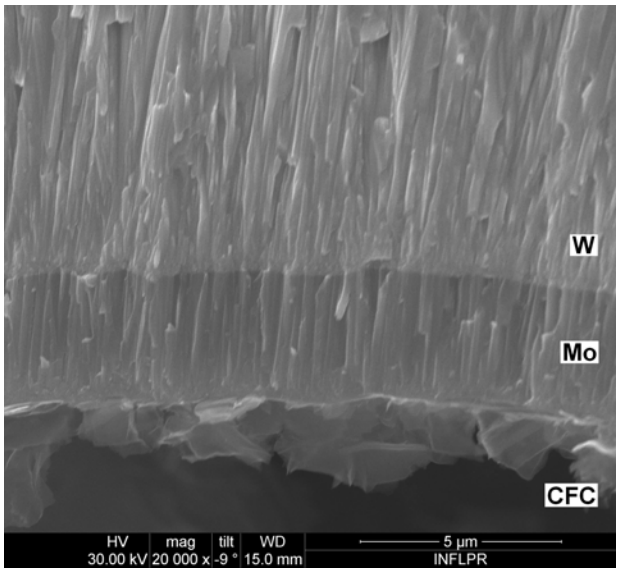


Fig. 7 SEM image of the CFC-Mo and Mo-W interfaces before HHF tests (fracture of the coating)

If this process goes on at higher temperatures (1500-2500°C) (for example due to the fact that near to the region of interest appeared a delamination and the W chips are very hot) the number and dimensions of pores will increase significantly. The interfaces CFC-Mo, Mo-W and the MoC layer might be seriously damaged (Fig.5) and the carbon diffusion might be stopped or drastically reduced. The WC layer already formed above the MoC layer will remain isolated without possibility to be supplied with carbon from the substrate. The thermal stability of the tungsten carbides is not so high. Said El Mrabet, et al. [4] demonstrated that heating a WC_{1-x}/a-C film deposited on Si up to 1100 °C the structure of WC_{1-x} changes to W_2C and WC between 700°C and 900°C. Over 900°C WC decomposes gradually and at 1200 °C the dominant phase is W. If the substrate is a carbon material it can supply the necessary carbon producing a carbide structure at higher temperatures in accordance with the W-C phase diagram. In the case of W/Mo coatings deposited on CFC and subjected to high thermal loads the flux of carbon can be limited by the pores generated at the interfaces or by severe damage of the Mo interlayer. In this way the absence of the carbides near to the delaminated zone might be explained. At the same time the pores structure limits the heat transfer from the outer surface of the W coating to the substrate and the coating becomes hotter. This leads to an increase of the density and dimensions of the pores and locally small fragments of the coating are finally detached from the substrate.

It looks like the pores act as a diffusion barrier for carbon from CFC. The properties of this barrier depend on dimensions and density of the pores, which are time and temperature dependent. This complicates the transfer of the carbon from the CFC and formation of carbides. Kinetics of this process was investigated in other paper by heating the W coatings deposited by CMSII on CFC in a vacuum oven at different constant temperatures (1200°C and 1350°C) for 2, 5 and 20 hours [5]. For the temperature of 1200°C a total carbide layer of 6.5 μm was formed in 2 h and the thickness of that layer increased to only 8 μm for 20 h. This saturation could be associated with the pores diffusion barrier.

5. Conclusions

- The damage of the W coatings deposited on CFC substrate occurs gradually with the increasing number of heating pulses.
- 10 μm and 20 μm W coatings have been tested with more than 3100 pulses at peak temperatures of 1250°C and 1450°C. The pulse duration was 24 s. At 1250°C the total delaminated area of the W coating of 20 μm was about 1 % of the thermal loaded area while for coating of 10 μm this percentage was about 0.2 % only. By increasing the testing temperature to 1,450°C the percentage of the delaminated area increased to about 6% for 20 μm W coating and 1.2% for 10 μm W coating for a similar number of heating pulses.
- The thinner coatings have a better thermo-mechanical behavior than the thicker coatings.
- The damage of the W coatings occurs by buckling with the size of delaminated zones in the range of 50-500 μm.
- 20 μm W coating survived 5100 pulses at a peak temperature of 1000°C without any delamination.
- The nano-pores structure generated at the CFC-Mo and Mo-W interfaces during the HHF tests could play an important role in W coating degradation, but this subject should be investigated in more detail.

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