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H. Maier[1*], M. Rasinski[2], E. Grigore[3], C. Ruset[3], H. Greuner[1], B. Böswirth[1], G.F. Matthews[4], M. Balden[1], S. Lindig[1], and JET-EFDA contributors[*]

[1]*Max-Planck-Institut für Plasmaphysik, EURATOM Association, Garching, Germany*
[2]*Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw*
[3] *National Institution for Laser, Plasma and Radiation Phys., Association EURATOM-MEdC, Bucharest, Romania*
[4]*EURATOM/UKAEA Fusion Association, Culham Science Centre, Abingdon, UK*
* See annex of F. Romanelli et al, "Overview of JET Results",
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ABSTRACT

We performed investigations to determine the lifetime of tungsten coatings on carbon under high heat flux with respect to tungsten carbide formation. Tungsten coatings with a molybdenum interlayer were deposited by combined magnetron sputtering and ion implantation. These coatings were heat treated in a vacuum furnace. Subsequently the fraction of the coating thickness which had converted into carbide, was determined by focussed ion beam preparation and electron microscopy. This thickness was found to extend from 10μm to 18μm for heat treatments between 2 and 20 hours at 1350°C. Such coatings were then exposed to high heat flux pulses of 16.5MW/m² with pulse durations of 1.5s. A clear threshold behaviour was found: While after 2 hours of heat treatment no coating failure was found, the delaminated surface fraction was up to 5% after treatment for 5 hours and up to 25% after treatment for 20 hours at 1350°C.

1. INTRODUCTION

The actual combination of plasma facing materials to be applied in the international fusion reactor project ITER has never been investigated in an integrated operational test in a tokamak. For this reason in early 2005 the ITER-like Wall Project was launched at JET [1]. It was decided to install a divertor with a fully tungsten-clad surface [2]. One toroidal row will be bulk tungsten tiles [3]. Re-engineering of the whole divertor with respect to the tile material was, however, not feasible within the given time frame. Therefore an industrially applicable solution for coating the original tile material with tungsten had to be found. This material is a bi-directionally Carbon-Fibre reinforced Carbon (CFC) [4-7].

For this purpose a large coordinated research and development project was implemented comprising several Euratom associations [8,9]. The outcome of this project was the decision to apply vacuum plasma sprayed tungsten coatings with a thickness of 200 μm for the divertor tiles. This was based on results from relatively small test tiles. It turned out that an upscaling of this coating process to full-size divertor tiles led to failures of the coatings in high heat flux testing [10]. For this reason the divertor tiles are coated by combined magnetron sputtering and ion implantation (CMSII), the other successful choice from the R&D project. These coatings have a thickness of only 10-25 μm including a 3 μm Mo interlayer.

One consequence of this choice is the fact that the JET divertor tiles do not possess a dedicated barrier against the formation of tungsten carbide in the coatings. The vacuum plasma sprayed tungsten coatings by Plansee SE are equipped with a rhenium/tungsten multilayer at the coating-substrate interface. This is a patented solution for suppressing the excessive formation of brittle tungsten carbide [11].

The purpose of this contribution is to investigate the rate of formation of tungsten carbide and its influence on the thermomechanical performance of the coatings in high heat flux tests.

2. THE W/C AND MO/C SYSTEMS

Tungsten is a refractory metal with the highest melting point of all metals. The solubility of carbon in tungsten is extremely low peaking at 2700°C with only 0.7 at.% [12].Tungsten and carbon can form metallic carbides: Tungsten di- or subcarbide W_2C and tungsten mono carbide WC. Depending on temperature the subcarbide has a wider existence range in terms of carbon content than the mono carbide. According to recent data, however, W_2C is thermodynamically unstable below a temperature of 1250°C [13]. (Additionally there is a high temperature phase WC_{1-x}.)

The molybdenum/carbon phase diagram is very similar to that of tungsten and carbon with respect to the carbob solubility. Here the maximum solubility of carbon in the metal lattice is 1.1 at.% at a temperature of 2205°C [14]. According to this reference there is no stable MoC phase above 1220°C.

The onset of the formation of tungsten subcarbide and carbide seem to depend on the spatial scale of the probing experimental setup: Leroy et al investigated the occurrence of these reactions at a carbon/tungsten interface by X-ray diffraction [15]. Upon heating of the sample they found the onset of tungsten subcarbide formation at a temperature in the range of 920°C - 970°C. The formation of tungsten mono carbide was observed to begin at 1050°C – 1100°C. Luthin and Linsmeier probed the presence of the respective tungsten carbide phases by X-ray photoelectron spectroscopy [16], which is a method with extreme surface sensitivity. Actually it probes only the first few monolayers of a material surface. Consequently they found the onset of the subcarbide and carbide formation at the somewhat lower temperatures of 500°C and 700°C, respectively.

In an experimental setup very similar to the latter one mentioned in the above paragraph, Reinke et al. observed the formation molybdenum carbide Mo_2C to occur already at 400°C [17]. Diffusion coefficients for the diffusion of carbon in tungsten and molybdenum for the temperature range required here can be found in [18]. The thickness growth of tungsten carbide phases in our coatings, however, requires the transport of carbon from the substrate through the already existing carbide zones to the carbide/metal interface. In such a situation self diffusion of carbon in tungsten carbide must be considered [19]. Schmid and Roth [20] observed a strong change of the carbon diffusion coefficient in the tungsten/carbon system as a function of carbon concentration. They report about distinct changes around the carbon concentrations which correspond to the existence ranges of tungsten carbide and subcarbide in thermodynamic equilibrium. Therefore data on carbon self diffusion in the respective tungsten carbide system are required. References [19] and [21] give such information including activation energies. They do so, however, only for temperature ranges above those considered here. Additionally it must be kept in mind that the carbon transport from the carbon substrate to the carbide/metal interface may be enhanced by grain boundary diffusion.

According to [17] there is no significant carbon diffusion barrier performance of Mo2C at elevated temperatures. One can therefore assume that the change in diffusion coefficient with carbon content is not as strong as the one for tungsten discussed above.

Given the situation described above and additionally the lack of detailed information about the

kinetics of the several individual solid state phase transformations necessary for the carbide growth in our tungsten coatings, the acquisition of dedicated data for the specific system under investigation here is considered to be necessary.

3. EXPERIMENTAL PROCEDURES AND DEVICES

The deposition of the coatings was performed at the National Institute for Laser, Plasma and Radiation Physics (NILPRP) in Bucharest, Romania. The coatings were deposited on bi-directionally carbon-fibre reinforced carbon Dunlop DMS780 substrates by the method of combined magnetron sputtering and ion implantation [22]. A molybdenum interlayer of 5 approximately 3-4 μm was applied and the coatings had a total thickness of 25-30 μm. The deposition was performed in the industrial size coating unit designed and constructed for the coating of the full-size JET tiles. The deposition chamber has a size of 800mm×750mm and is equipped with 24 magnetrons [23]. For the ion implantation high voltage pulses of $U= 30–50$ kV are applied with a typical duration of 20 μs and a repetition rate of f = 25 Hz. A DC bias of up to −900V is applied additionally between pulses. The coated tiles were subsequently heat treated at Forschungszentrum Jülich, Germany, with several hold times to achieve a variable degree of carbidisation. This conditioning was performed at 1350°C in a high vacuum furnace at pressures ranging from $7*10^{-5}$ mbar to $2*10^{-6}$ mbar during the heat treatment. Two pairs of tiles were treated with dwell times of 20 hours and 5 hours, respectively. One individual tile was processed for 2 hours.

These sets of tiles were then pre-characterised and tested in the high heat flux facility GLADIS [24,25]. GLADIS is a facility with two RF ion sources with a beam power output of up to one MW each. The beams are of Gaussian shape with a typical 80% width of 7-8 cm. High heat flux testing was performed at a central beam power density of 16.5 MW/m² and a pulse duration of 1.5 s. A combination of a rather short pulse duration with a high power density gives high peak surface temperatures at a low energy input allowing for fast pulse repetition by minimising the cool-down time in between pulses.

For an analysis of the thickness of the carbide layer in these tiles cross sections of the coatings were fabricated by focussed ion beam (FIB) cutting through the coating at an angle of 52° to the surface normal in a dual beam FEI HELIOS NanoLab 600 machine with a maximum acceleration voltage of 30 kV. It is then possible to obtain a contrast in SEM imaging allowing the distinction between the different phases in the sample [10]. A direct identification of the various visible phases was performed by transmission electron microscopy [26]. This way the thickness of the carbide layer can be determined in the carbidised samples without macroscopic damage to the sample, i.e. even before high heat flux testing.

For a further assessment of the growth kinetics of the carbide films small samples with dimensions of approximately 10 mm*10 mm*1 mm were produced and subjected to a heat treatment at 1200°C in an inert gas furnace. From these also FIB cross sections were analysed, see section 4.2. An example for a focussed ion beam cross section is shown in figure 1.

4. RESULTS AND DISCUSSION

4.1 APPEARANCE AFTER HEAT TREATMENT

After the heat treatment described in section 3 only the tile treated for 2 hours had a delamination-free coating. There was a clear ranking in the apparent degree of damage for the three dwell times: While the tile heat treated for 2 hours was defect-free, the delaminated coating area fraction clearly increased when the dwell time was increased from 5 hours to 20 hours. It must be mentioned, however, that there was also a distinct difference visible between the two tiles of each respective dwell time pair for the 5 and 20 hour samples.

The observed failures give a strong indication for thermal expansion mismatch and brittleness of the grown carbide layers as reasons for the failure. An additional reason may be the increase in volume density upon transformation from tungsten to the carbides [27]. An increase of the lattice parameter with increasing carbon content is reported in [13] for the high temperature phase WC_{1-x}. Such phenomena can create an additional isotropic compressive stress component, which would be beneficial in the direction of tensile stress for the coating, i.e. along the fibres, but would increase the compressive stress in the other surface direction. A discussion of the direction-dependent stresses due to the thermomechanical mismatch of coating and substrate can be found in [8].

4.2 KINETICS OF CARBIDE FORMATION

Figure 2 A) shows the total thickness of the grown carbide layers as a function of dwell time for the full tiles heat treated at 1350°C and for the small samples treated at 1200°C, see section 3. In figure 2 B) the same data are shown in a normalised way, see caption. As can be seen the 1200°C data show a faster initial growth of the carbide layer thickness than the 1350°C data. For longer times, i.e. 300 - 1200 minutes both data sets seem to develop similar kinetics. For simple thermally activated processes one would expect a faster growth at the higher temperature for all times. Possible reasons for this peculiar time dependence could be:

• Different microstructure and chemistry: According to the phase diagrams discussed in section 2 ([13,14]) both, molybdenum carbide and tungsten carbide, show one phase that has a lower limit of thermodynamic equilibrium existence which is just in between the two selected temperatures. This assumption is however in contradiction to the information on temperatures of formation given in references [15] and [16]. Any other difference of micro structure and/or –chemistry not discussed here could also cause different rate-limiting processes in the various phases at the two different hold temperatures.

• Influence of sample size on heating rate: While the small samples treated at 1200°C were heated to their hold temperature rather rapidly (3-4 minutes from 400°C to 1200°C), it takes considerably longer to heat the full test tiles to 1350°C. In our case it took typically two hours. This is a difference which should systematically occur for short hold times and disappear for very long ones, which would be in agreement with observation.

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4.3 HIGH HEAT FLUX TESTS OF CARBIDISED TEST TILES

The carbidised tiles were high heat flux tested at a central power density 16.5 MW/m^2 with a pulse duration of 1.5s.

The tiles with the strongest pre-damage, i.e. those heat treated for 20 hours were subjected to 25 high heat flux pulses. They showed strong further delamination and melting along the edges of delaminated areas accompanied by a distinct particle release. To characterise the damage growth in a semi-quantitative fashion the apparent averaged surface temperature as measured by the infrared camera system was used. Since there is a strong difference in emissivity between tungsten and carbon, this is a very sensitive measure for the fraction of delaminated surface area. Of course this necessarily means that the given temperatures cannot be interpreted as such. The data show no significant increase after 25 pulses, which means that further delamination of coating had slowed down considerably after this number of pulses. For the resulting delaminated surface area fraction se table 1. A surface temperature measurement by pyrometry was not possible for this pair of tiles.

The pair of tiles heat treated for 5 hours also showed growing delaminated areas and melting along their edges. The extent of that was however much less than described above. Here a heat loading of 50 pulses was carried out. Again the evaluation of the infrared camera frames indicates that further damage had slowed down considerably. Also here surface temperature measurement by pyrometry was not possible

The tile heat treated for 2 hours was heat loaded with 50 pulses reaching peak surface temperatures around 1400°C. It was then removed from the high heat flux facility and subjected to microscopy examination of the coating. No delamination was observed. Subsequently the tiles was exposed to another 150 heat load pulses. In a second examination by microscopy one individual microscopic delamination failure was observed. It can be summarised that a clear threshold behaviour was observed with respect to delamination damage of carbidised coatings. The quantitative results on delaminated surface area fractions are listed in table 1.

CONCLUSION

The results presented in section 4.3 clearly show that delamination of large surface fractions of the tungsten coatings can occur in high heat flux tests after a carbidisation heat treatment. For a treatment at 1350°C the observed delaminated surface area fractions as a function of dwell time are the following :

- Up to 25% after 20 hours
- Up to 5% after 5 hours
- 0.02% after 2 hours.

The data indicate that upon successive increase of the carbidised coating fraction this type of failure will start to show with very small-scale delaminations. This is also supported by preliminary results on thinner coatings presented in reference [10]. The results suggest that it should then be possible

to control further damage growth by restricting the peak surface temperature. Clearly regimes corresponding to the above heat treatments of 5 or more hours should be avoided.

Since the delamination damage displayed a distinct threshold behaviour, a tool for predicting at which point in the ITER-like Wall experiment this critical carbidisation level will be reached is highly desirable. Given the facts observed during this work combined with the survey of literature information, we think that such a tool should rather be based on a pragmatic approach deduced from an empirical analysis of experimental data rather than a thorough thermodynamic modelling of the situation occurring during JET pulses.

It is well known that in JET relatively large edge-localised modes can occur [28]. The effect of those on the thermomechanical performance of carbidised tungsten coatings has so far not been assessed in the frame of the ITER-like Wall Project.

ACKNOWLEDGEMENTS

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Dwell time	2 hours	5 hours	20 hours
Delaminated fraction	0.02%	1%, 5%	18%, 25%

Table 1: Observed delaminated surface area fractions for the respective dwell times after vacuum heat treatment at 1350°C.
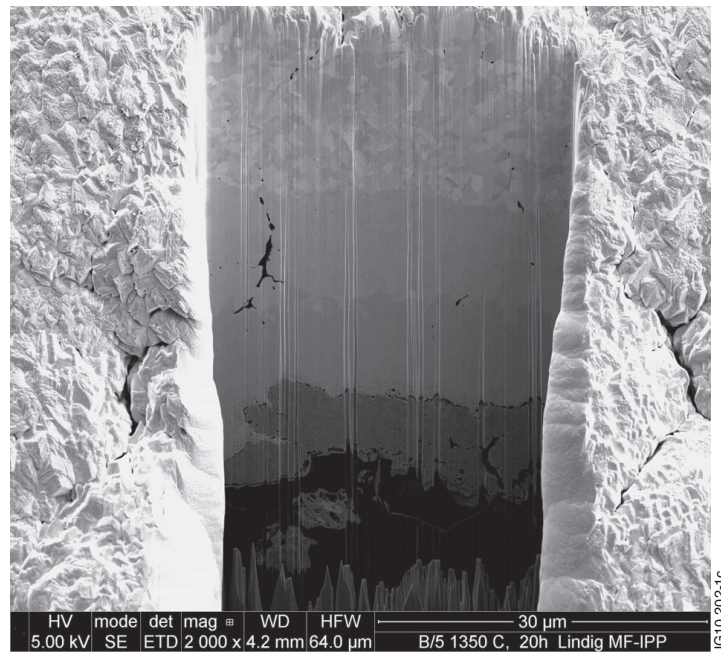
Time (s)

Figure 1: SEM image of a cross section cut by a focussed ion beam into the coating surface at an angle of 52° to the surface normal viewed with an electron beam in surface normal direction. On the bottom of the trench some remaining needles from the sputtered coating are visible. The areas to the left and right correspond to the original surface. The cross section shows from bottom to top: Molybdenum carbide, tungsten carbide, tungsten subcarbide, and remaining tungsten.
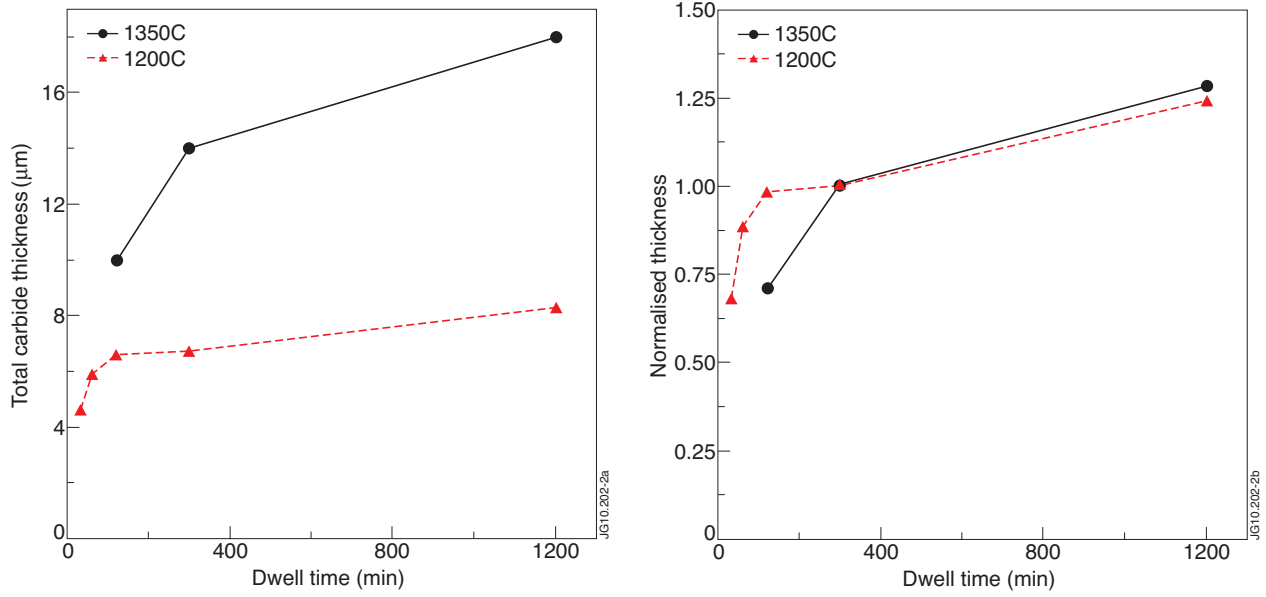
Figure 2: A) Total thickness of carbidised coating fraction including the molybdenum carbide as well as both types of tungsten carbide. The data from the small samples treated at 1200°C as well as those from the full tiles treated at 1350°C are shown. B) Same data as above with a normalised thickness axis such that the data sets coincide at a dwell time of 300 minutes.