Kinetics of carbide formation in the molybdenum-tungsten coatings used in the ITER-like Wall

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Abstract
The kinetics of tungsten carbide formation was investigated for tungsten coatings on CFC with a molybdenum interlayer as they are used in the ITER-like Wall in JET. The coatings were produced by combined magnetron sputtering and ion implantation. The investigation was performed by preparing focused ion beam cross sections from samples after a heat treatment in argon atmosphere. Baking of the samples was done at temperatures of 1100°C, 1200°C, and 1350°C for hold times between 30 minutes and 20 hours.
It was found that the data can be well described by a diffusional random walk with a thermally activated diffusion process. The activation energy was determined to be (3.34±0.11) eV. Predictions for the isothermal lifetime of this coating system were computed from this information.

1. Introduction

Tungsten will be used as plasma-facing material on the divertor targets of ITER [1]. Therefore one objective of the ITER-like Wall experiment at JET is to apply tungsten also as plasma-facing material in the divertor of JET. Except for one toroidal row of solid tungsten the employed solution is a tungsten coating of the Dunlop carbon fibre composite (CFC) divertor tiles [2]. This 10-25 µm thick coating was deposited by combined magnetron sputtering and ion implantation (CMSII) [3] together with a 3-4 µm thick Mo interlayer for mitigating coating stress and thermal expansion problems [4].

Both molybdenum and tungsten are carbide forming metals. Therefore the employed materials combination will lead to diffusion of carbon atoms from the substrate material into the metals and subsequently to metal carbide formation at elevated temperatures. As tungsten and its carbides are technologically important materials for application especially at high temperatures, the kinetics of the process was investigated in a number of publications, e.g. [5, 6, 7].

Like the carbides of several transition metals, tungsten and molybdenum carbide are brittle ceramic materials. The progressive formation of tungsten carbides in tungsten coatings on carbon substrates is known to finally cause failure of the coating in high temperature application. For this reason a W/Re interlayer system to suppress the in-diffusion of carbon from the substrate into the tungsten layer was developed and patented in the early 1990s mainly for application in X-ray rotating anodes [8]. In the frame of the ITER-like Wall this

interlayer system was investigated; however its use had to be abandoned due to problems with the oxidation behaviour of Re [9].

Since the CFC/molybdenum/tungsten layer system described above is not equipped with such a diffusion barrier, high heat flux tests were carried out in the GLADIS high heat flux facility [10] to determine the stability of the coatings system after heat treatment. Several samples with a 25 µm W coating were pre-treated by baking at 1350°C in a vacuum furnace. A threshold-like result was observed in subsequent high heat flux testing at 16.5 MW/m² with beginning coating delamination after a hold time of 5 hours corresponding to a carbide layer thickness of about 15 µm [11].

In this contribution we investigate and analyse the kinetics of the formation of carbides in the CFC/Mo/W system employed in the ITER-like Wall at JET. We determine the carbide layer thickness as a function of temperature and time. From the analysis of this dataset we identify the kinetic parameters determining the progressive formation of carbides in the system specific for the ITER-like Wall at JET.

2. Experiment

The experiments were presented in detail in [12, 13]. Here we give a brief description:

CFC tiles were coated with a 2-4 µm thick Mo interlayer and subsequently with a 10 µm W film at the National Institute for Laser, Plasma and Radiation Physics in Bucharest employing the CMSII technique. These were cut into samples with dimensions 10×10×3 mm³ and annealed in Argon atmosphere at temperatures of 1100°C, 1200°C, and 1350°C for hold times between 30 minutes and 20 hours.

The samples were subsequently investigated by preparing a cross section of each sample in a dual beam device combining focused ion beam and scanning electron microscope. From these cross sections the thicknesses of the individual carbide layers was determined. An example of such a cross section is shown in figure 1.

The quantity to be further analysed in this contribution is the total thickness of the tungsten carbides, i.e. the sum of the layer thicknesses of the WC layer and of the W_2C layer. This quantity is displayed in figure 2 for all investigated temperatures and hold times.

The carbide formation in the Mo interlayer is neglected in the further analysis. Even at the lowest baking temperature this process is already completed after the shortest hold time of our experiments.

3. Data analysis

If we restrict the data analysis to times longer than one hour and allow a free parameter for an offset value, the total layer thicknesses shown in figure 2 can rather well be described by the relation

$$x(T)^2 = \boldsymbol{D}(T) \times t \qquad (1)$$

with $\boldsymbol{x}$ being the total W carbide layer thickness a specified in the experimental part, $\boldsymbol{D}$ the rate constant and $\boldsymbol{t}$ the hold time. This represents the typical random walk behaviour which is expected for a diffusional process, see e.g. [14]. Therefore the rate constant can be interpreted as a diffusion coefficient describing the diffusional progression of the reaction front, i.e. the interface W_2C/W. Diffusion in solids is a thermally activated process. Therefore if we can identify $\boldsymbol{D}$ with a diffusion coefficient, then its temperature dependence should – in the simplest case – be represented by an Arrhenius expression [15]:

$$\boldsymbol{D}(T) = \boldsymbol{D_0} \times \exp\left(-\frac{\boldsymbol{E}}{kT}\right) \qquad (2)$$

with $\boldsymbol{D_0}$ being a frequency factor and $\boldsymbol{E}$ the activation energy of the process. The traditional way to test experimental data for this relationship is to plot the logarithm of the diffusion coefficient versus the reciprocal absolute temperature. If the relation (2) is a good description for the data, then this plot should allow to fit the data with a straight line. As described in section 2 we have time-dependent data for three different temperatures. This means that we can fit the data according to equation (1) for the three temperatures separately and obtain three values for the diffusion coefficients $\boldsymbol{D}$ to test for an Arrhenius behaviour. The result of this procedure is plotted in figure 3. As can be seen, the data are well represented by an Arrhenius behaviour. Therefore we can consider the assumption of a Boltzmann-like model description of the temperature dependence to be appropriate.

To obtain the pair of ($\boldsymbol{D_0}$, $\boldsymbol{E}$) values which yields the best fitting description of the measured data points and error bars within our model we calculated the likelihood distribution p($\boldsymbol{D_0}$,$\boldsymbol{E}$|data) [16] of the parameter space. Computing mean and variance for D_0 and E from the resulting probability distribution we obtain:

$$D_0 = (5.3 \pm 2.6) \times 10^{-5} \frac{m^2}{s} \text{ and}$$

$$E = (3.34 \pm 0.11)\ eV \qquad (3)$$

4. Discussion

Carbide layer growth

We can compare our results with literature data referring to the diffusion of carbon in tungsten carbide, references [5] to [7]: references [5] and [7] deal with tungsten wires heated in hydrocarbon atmospheres as a carbon source, while reference [6] refers to ^{14}C diffusion in tungsten carbide specimen hot pressed from powder. The activation energies from these references are given in table 1. All three references identify the mentioned activation energies with the diffusion of carbon in tungsten carbide. In contrast to this, reference [17] gives significantly smaller values between 1.6 eV and 2.1 eV quoting 5 different sources for the diffusion of carbon in pure tungsten. We can therefore identify the progressive growth of tungsten carbide layers in our coatings as a diffusion/reaction process with the diffusion of carbon in tungsten carbide as the rate-limiting process.

Consistently the activation energy given in the literature for the diffusion of carbon in molybdenum carbide of 2.5 eV [18] is significantly lower.

As the cross section in figure 1 shows, there are two different tungsten carbides present in our samples. From our data we cannot unambiguously deduce whether it is the WC or the W_2C phase, which constitutes the growth rate limitation. This does, however, not affect the analysis presented above.

Isothermal lifetime

Using the model constituted by equations (1) and (2) together with the data (3) we can estimate the carbide layer thickness for any given temperature in the isothermal case. If we assume the thickness of the tungsten layer consumed by carbide formation to be the quantity limiting the lifetime of the coating during service, we have to specify a limiting carbide layer thickness to determine a coating lifetime from the model. This was investigated experimentally in [11] for a tungsten coating thickness of 25 µm: several tiles were baked in a vacuum furnace for hold times of 2 hours, 5 hours and 20 hours to achieve different thicknesses of tungsten carbide in the coatings, which were determined by focused ion beam cross sectioning. Subsequently they were high heat flux loaded in GLADIS at 16.5 MW/m² for 1.5 s with up to 200 pulses. With respect to coating delamination a threshold-like result was obtained from these tests. For further details see [11]. Based on these experimental results we assume here that the coatings reach their service lifetime, when a carbide layer thickness of 15 µm is exceeded.

Using (1)-(3) we can now compute for the isothermal case what would be the expected lifetime as a function of temperature. This plot is shown in figure 4. Please note the logarithmic ordinate. For comparison the limits for thresholds of 10 µm and 20 µm are also shown. Since the employed threshold value of 15 µm is based on very few experimental results, the 10 and 20 µm limits can be used for illustrating the sensitivity of the estimate to this value.

As the figure shows, the expected isothermal lifetime drops by six orders of magnitude, when the temperature is increased from 1000°C to 2000°C. This is due to the fact that the diffusion process, which is the rate-limiting element, is a thermally activated process, the rate of which depends exponentially on the temperature. The additional data shown for limits of 10 µm or 20 µm, respectively, illustrate that this statement is not very sensitive to the actually chosen threshold value. As our analysis shows, it is also not very sensitive to the precise values of the parameters of equation (3).

This illustrates qualitatively that the peak surface temperatures occurring in JET discharges can have a significant influence on the lifetime of the tungsten coatings on CFC tiles in the divertor.

5. Summary

Due to problems with the oxidation behaviour of Re the tungsten coatings on CFC tiles employed in the ITER-like Wall at JET are not protected against carbide formation. It has been shown experimentally that the formation of tungsten carbide eventually leads to failure of the coating under high heat flux loading. For this reason the kinetics of the tungsten carbide formation was investigated for the specific system used in JET, i.e. tungsten coatings with a molybdenum interlayer deposited on Dunlop CFC by combined magnetron sputtering and ion implantation.

It was shown that the long-term behaviour of the progressing carbide formation process can be described as a diffusional process with a temperature dependence represented by a Boltzmann factor. From the corresponding data analysis a frequency factor and an activation energy were deduced. These were employed to compute the isothermal lifetime of the tungsten coating assuming a failure threshold of carbide layer thickness.

This assessment shows that the expected isothermal lifetime of the coating is strongly temperature dependent and drops by six orders of magnitude when the temperature is increased from 1000°C to 2000°C. For an estimate of the coating lifetime in JET operation an evaluation involving time dependent temperatures is necessary. The analysis presented here is a first step in this direction. In addition adhesion failure of the coatings on CFC can also depend on parameters other than the carbide formation analysed in this contribution.

Table 1: comparison of the obtained activation energy with literature data.

Source	[5]	[6]	[7]	this work
Value	4.6 eV	3.8 eV	3.3 eV	3.4 eV

References

[1] M. Merola et al. 2014 Fus. Eng. Des. 89 890

[2] G. F. Matthews et al. 2007 Phys. Scr. T128 137

[3] C. Ruset et al. 2007 Phys. Scr. T128 171

[4] C. Ruset et al. 2011 Fus. Eng. Des. 86 1677

[5] M. R. Andrews and S. Dushman 1925 J. Phys. Chem. 29 462

[6] C. P. Bushmer, P. H. Crayton 1971 J. Mater. Sci. 6 981

[7] S. L. Kharatyan, H. A. Chatilyan L. H. Arakelyan 2008 Mat. Res. Bulletin 43 897

[8] European Patent EP 0 399 621 B1, 1993

[9] H. Maier et al. 2009 Phys. Scr. T138 014031

[10] H. Greuner et al. 2007 J. Nucl. Mater. 367–370 1444

[11] H. Maier et al. 2011 J. Nucl Mater. 415 S310

[12] M. Rasinski IPP report 17/36, Max-Planck-Institut für Plasmaphysik, 2012 - M. Rasinski Dissertation Warsaw University of Technology 2012

[13] M. Rasinski et al. 2013 Thin Solid Films 531 21

[14] H. Mehrer, "Diffusion in Solids", Springer Series in Solid State Sciences 155, Springer Berlin 2007

[15] M. E. Glicksman, „Diffusion in Solids", John Wiley and Sons, New York 2000

[16] W. von der Linden, V. Dose, U. von Toussaint, „Bayesian Probability Theory", Cambridge University Press 2014

[17] O. Madelung (ed.), Landolt-Börnstein New Series Vol. III/26, "Diffusion in Solid Metals and Alloys", ed. H. Mehrer, Springer Berlin 1990

[18] Y. Isobe et al. 1989 J. Less-Common Metals 147 261

Figure captions:

Figure 1:

Example of a scanning electron microscope image of a focussed ion beam cross section taken from a sample after heat treatment. The image shows in different grey scale levels from bottom to top: CFC substrate, Mo carbide, WC, W_2C, W.

Figure 2:

Total tungsten carbide layer thicknesses as a function of hold time for three different temperatures.

Figure 3:

Arrhenius plot of the diffusion coefficients measured at the three different temperatures. The solid line indicates that the data can be well described by a thermal activation term.

Figure 4:

Computed isothermal coating lifetime as a function of temperature assuming a failure threshold of 15 µm of carbide layer thickness. The sample is assumed to be at constant temperature for the whole time. For comparison the durations to grow 10 µm and 20 µm of tungsten carbide are also plotted. Please note the logarithmic ordinate.

Figure 1

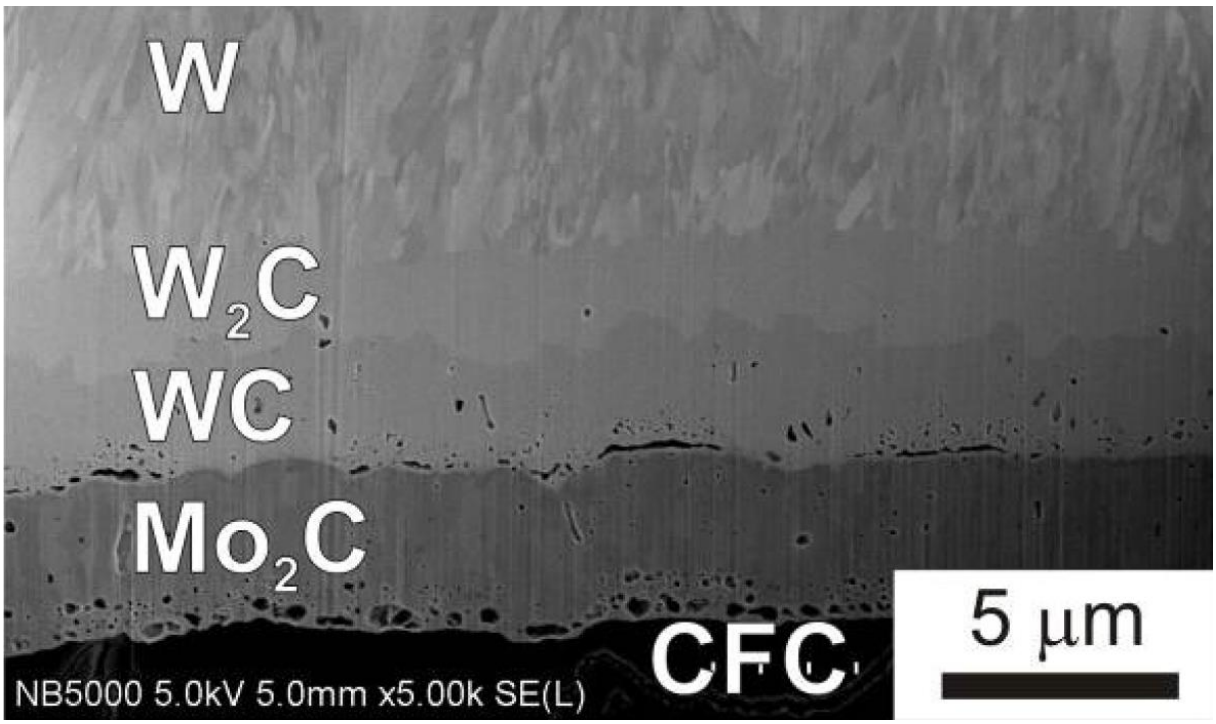


Figure 2

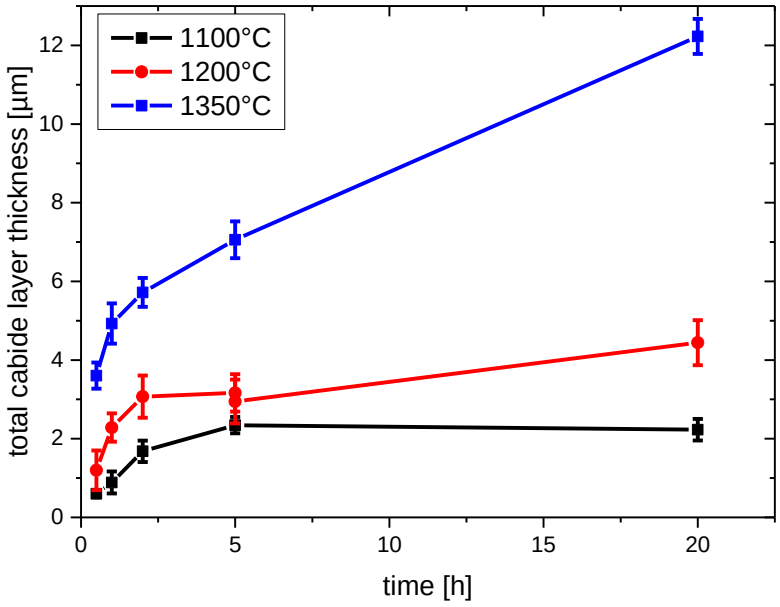
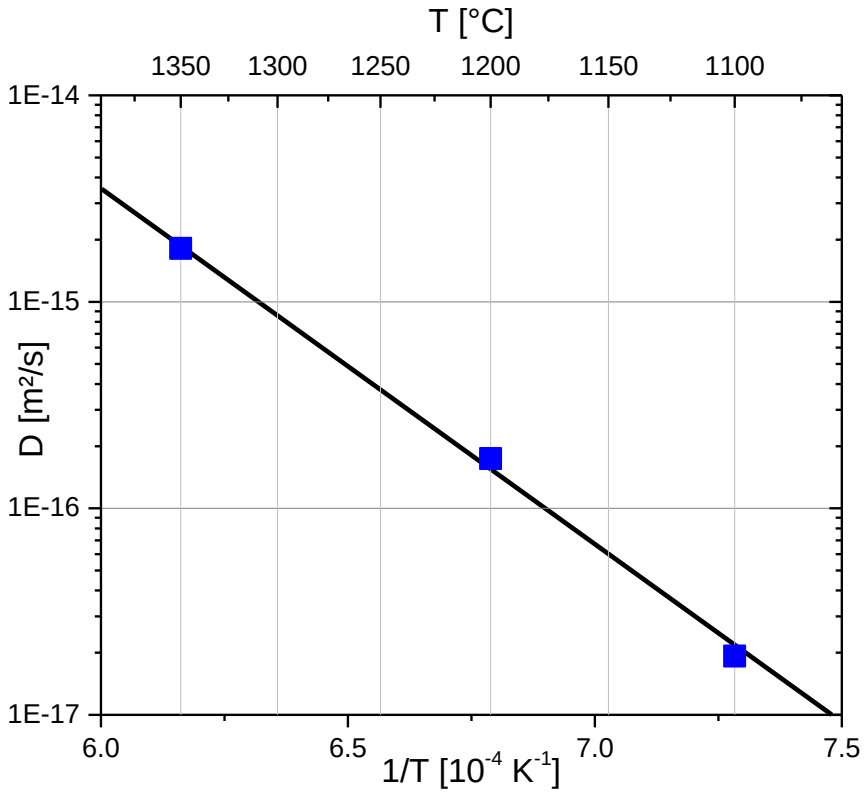


Figure 3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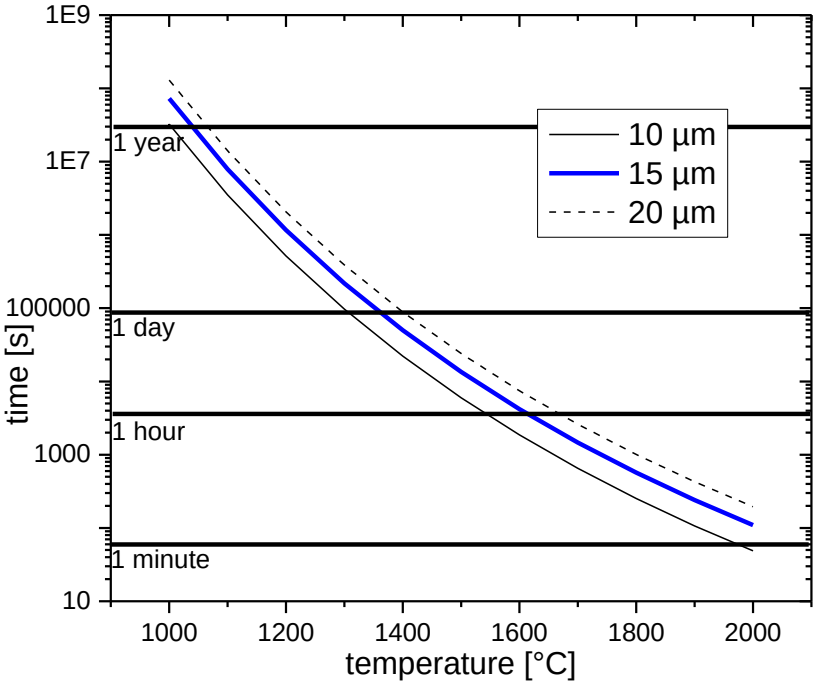
1300
1250
1200
1150
1100
1E-14
1E-15
1E-16
1E-17
D [m²/s]
6.0
6.5
7.0
7.5
1/T [10⁻⁴ K⁻¹]

Figure 4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