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High-temperature properties of joint interface of VPS-tungsten coated CFC

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Abstract

Tungsten coated carbon fiber composite (CFC) is a candidate material for the high heat flux components in fusion reactors. In order to investigate the high-temperature properties at the joint interface of coating, heat load experiments by using electron beam were performed on VPS-tungsten coated CX-2002U samples. After the heat load test for 3.6 ks at 1400 °C, tungsten–rhenium multilayer (diffusion barrier for carbon) at the joint interface of coating was observed clearly. But, at the temperatures above 1600 °C, the multilayer was disappeared and a tungsten carbide layer was formed in the VPS-tungsten coating. At the temperatures below 1800 °C, the thickness of this layer logarithmically increased with increasing its loading time. At 2000 °C, the growth of the tungsten carbide layer was proportional to the square root of loading time. These results indicate that the diffusion barrier for carbon is not expected to suppress the carbide formation at the joint interface of the VPS-tungsten coating above 1600 °C.

1. Introduction

Tungsten and its alloys are considered as candidate materials for high heat flux components such as limiter blocks and divertor tiles in fusion experimental devices because of their good thermal properties and the low sputtering yield. However, tungsten has the disadvantages of brittleness below 400 °C and of heaviness. In order to overcome these disadvantages, thin tungsten coating on light materials with high melting point such as carbon-based materials is considered as advanced high heat flux materials [1]. In the present study, we prepared tungsten coated CFC specimens by a vacuum plasma spray (VPS) method and examined their thermal behavior high-temperature (>1300 °C).

VPS-tungsten coated graphite limiters have been used in TEXTOR [2,3], and it was reported that some of those limiters were seriously damaged during the discharge experiments. Especially, the top surface of the poloidal limiters suffered very severe damages such as cracking, removing and melting by high heat flux of the TEXTOR plasma. But, as reported in Ref. [4], a small piece (20 mm × 20 mm × 10 mm) of this material showed good heat load resistance in the heating condition up to 2800 °C at the coating surface. It is very important for the limiters in the experimental apparatus that they can keep reasonable properties even after the unexpected severe heat loads which may heat the limiters up to high-temperature.

Tokunaga et al. analyzed the initial composition in the cross-section of the joint interface of VPS-tungsten coated CFC material by using an electron probe microanalyzer (EPMA) [5]. According to their results, the first PVD-tungsten layer in the multilayer contains carbon (C) of 40 at.% and the area of the near joint interface of

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the VPS-tungsten layer contains C of 10 at.%. They thought that the carbon diffusion from the CFC substrate occurred during the heat treatment at 1300 °C after the coating process. The lifetime of this coating is limited by carbide formation, which leads to a considerable decrease in thermal conductivity, resulting in large temperature increase, subsequent embrittlement of the coating and cracking or melting [6].

Therefore, we focused in the present work on the metallurgical change of the joint interface. Then, annealing experiments (1400–2000 °C) were performed on the VPS-tungsten coated CFC material to investigate the diffusion behavior at the joint interface.

2. Experimental

2.1. Specimen

The sample of VPS-tungsten deposited on CX-2002U substrate (prepared by Toyo Tanso) was produced by Plansee Aktiengesllshaft. The CX-2002U received PVD-multilayer diffusion barrier layers of rhenium and tungsten prior to the VPS-tungsten coating in order to inhibit uncontrolled brittle carbide formation [4]. The thickness of the VPS-tungsten coating layer was about 0.5 mm. After the coating, the VPS-tungsten coated CFC sample was treated at 1300 °C in a vacuum to stabilize the internal structure, and then was cut into pieces of 5 mm × 5 mm × 2 mm. For the purpose of calculating the average density of this VPS-tungsten coating, volume and weight were measured for the three pieces. As a result, average density of this VPS-tungsten is 85% of the theoretical value.

2.2. Annealing conditions

The specimens were heated with a uniform electron beam by using the Electron Beam Irradiation Test Simulator at Research Institute for Applied Mechanics, Kyushu University [7]. The energy of the electron beam was 20 keV and its current was adjusted to obtain the desired temperature (heat flux: $\leqslant 0.8$ MW/m^2). Details of the heating conditions are summarized in Table 1.

2.3. Material test

The specimens were put on a horizontal holder made of tantalum to reduce thermal contact. The surface temperature of the specimen was measured with calibrated two color optical pyrometers (450–1100 °C, 1100–3100 °C). The internal structure was observed by a scanning electron microscopy (SEM). The compositional and structural change of joint interface after the annealing was examined with an X-ray diffractometer (XRD). The back surface of the coating was mechanically polished to the coating surface in regular incre-

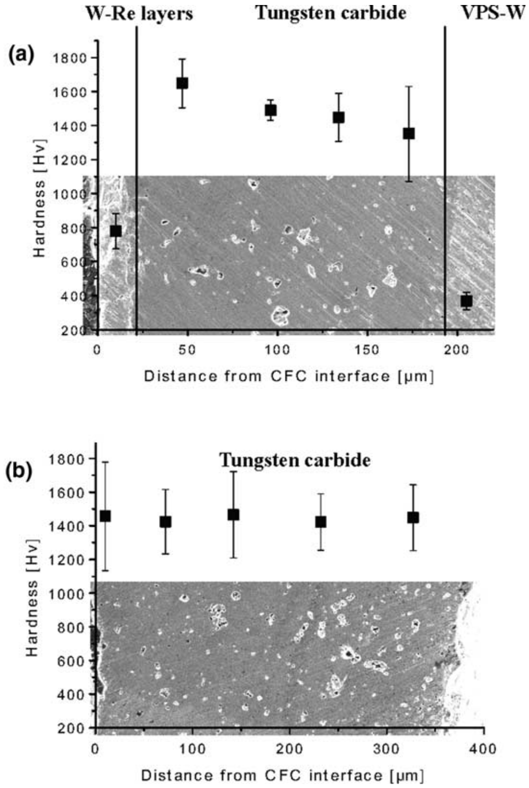

Fig. 1. The hardness distributions along the thickness direction from the joint interface after annealing for 3.6 ks at 1800 °C (a) and 3.6 ks at 2000 °C (b).

Table 1
The annealing conditions

Temperature [°C]	Annealing time [s]									
	60	300	600	1200	1800	2400	3000	3300	3540	3600
1400	–	–	–	–	–	–	–	–	–	●
1600	●	●	●	●	●	–	–	–	–	●
1800	●	–	●	–	●	●	●	●	●	●
2000	●	●	●	–	●	–	–	–	–	●

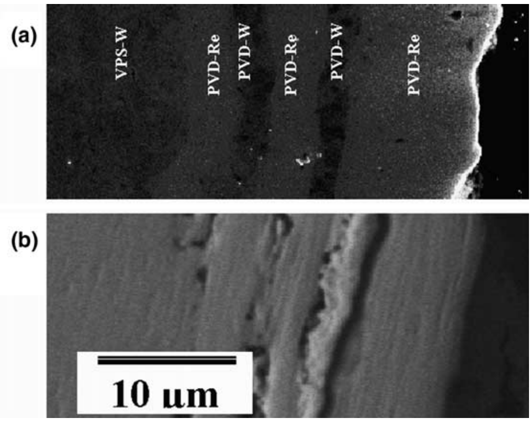

Fig. 2. SEM image (a) of the polished cross-section of the sample annealed for 3.6 ks at 1400 °C and backscattered electron (shadow) image (b).

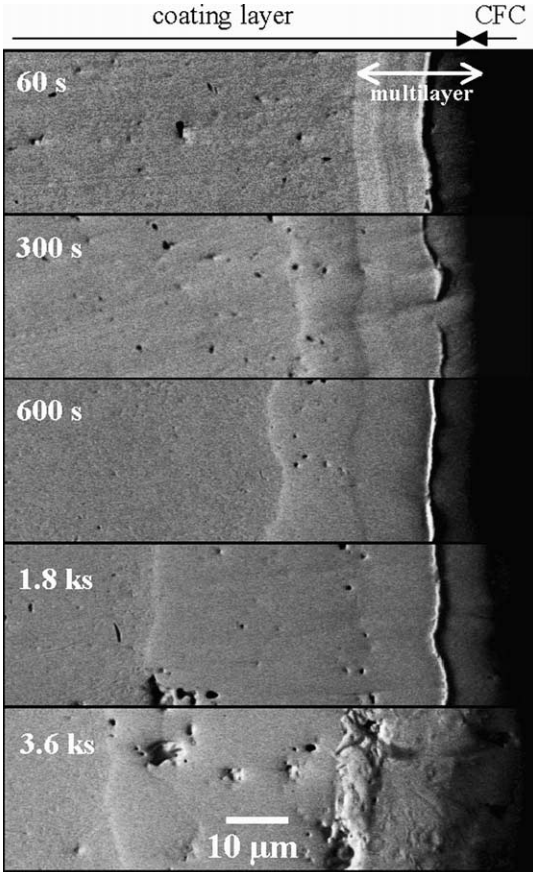

Fig. 3. Backscattered electron (shadow) images of the cross-section annealed for various annealing times at 1600 °C.

ments in order to measure the XRD in the thickness direction. The XRD measurements were performed using a goniometer at a scanning range of 10° ⩽ 2θ ⩽ 90° and stepwise by 0.05°. Micro-Vickers hardness of the coating layer in a cross-section was also measured.

3. Results and discussions

3.1. Compositional changes in the VPS-tungsten coating

After annealing for 3.6 ks at 2000 °C, a new layer, which has large pores (these diameters are below 20 µm) was formed in the VPS-tungsten coating. It seems that those pores were formed due to the coalescence of the cavities which had been contained in the VPS-tungsten matrix. Fig. 1 shows the SEM images and the hardness distribution along the thickness direction of the polished cross-section of the samples annealed for 3.6 ks at 1800 and 2000 °C, respectively. The mean hardness of these new layers is greater than 1400 H_V. The results of XRD

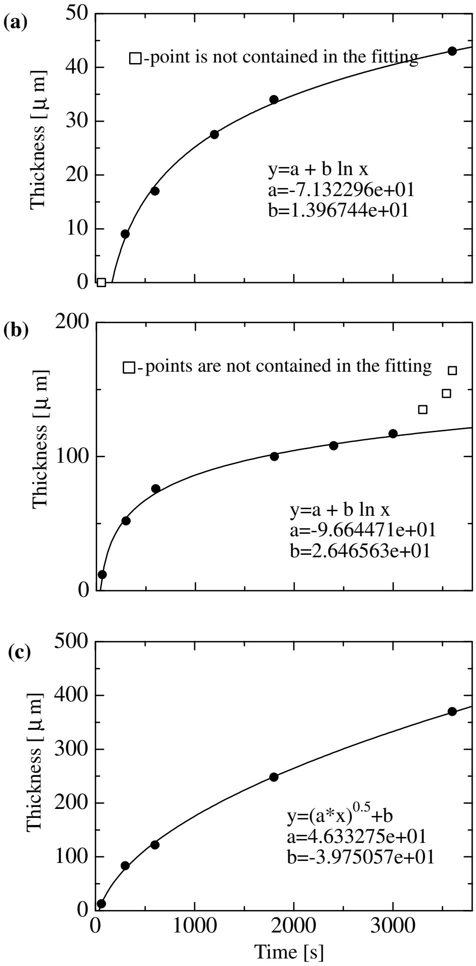

Fig. 4. Thickness increase of the tungsten carbide layer as a function of annealing time at 1600 °C (a), 1800 °C (b) and 2000 °C (c).

analysis for these layers showed tungsten carbides (W_2C, WC).

3.2. Evolution and morphologies of carbide layer in the VPS-tungsten coating

Fig. 2(a) and (b) show the SEM image and the backscattered electron (shadow) image of the polished cross-section of the sample which was annealed for 3.6 ks at 1400 °C. The multilayer at the joint interface is still completely remaining. Generally, convexes are formed at harder surface by the mechanical polishing process. So, the dark region in the polished cross-section shown in Fig. 2(b) is a shadow due to the step in the multilayer. It can be said that the first layer from the joint interface is hardest in the multilayer due to the diffusion of carbon from the CFC substrate.

Fig. 3 shows the micrographs near the joint interface of the polished cross-section from the samples which were annealed in various annealing times, from 60 to 3600 s, at 1600 °C, individually. After the annealing for 60 s, the multilayer was observed clearly and any carbide layer was not observed in the VPS-tungsten coating layer. After the annealing for more than 300 s, however, the morphology of the multilayer was changed and a tungsten carbide layer was formed in the VPS-tungsten coating layer. The thickness of the layer increased with increasing annealing time. Fig. 4(a) shows the mean thickness of the tungsten carbide layer as a function of annealing time at 1600 °C. The fitted line in Fig. 4(a) indicates that, the increase of mean thickness is directly proportional to the logarithm of annealing time. This means that the atom (C) transmission in the layer at the joint interface is a rate-limiting step in this reaction sequence. The equation of the fitting line and parameters are denoted in the figure. Fig. 4(b) shows the increase of mean thickness of the tungsten carbide layer at 1800 °C. The increase of mean thickness is also directly proportional to the logarithm of annealing time within 3.3 ks. The logarithm-increase indicates that the joint interface acts as a diffusion barrier in the temperature range below 1800 °C. In contract, the samples annealed for more than 3.3 ks at 1800 °C, the thickness of tungsten carbide layer increased beyond the range of logarithmic law. It means that the effect of the joint interface as the diffusion barrier loss goes down at this annealing condition (above 3.3 ks at 1800 °C).

Fig. 4(c) shows the increase of mean thickness of the tungsten carbide layer at 2000 °C. The mean thickness is directly proportional to the square root of the annealing time. This means that the effect as diffusion barrier at the coating interface has completely lost. Growth of this

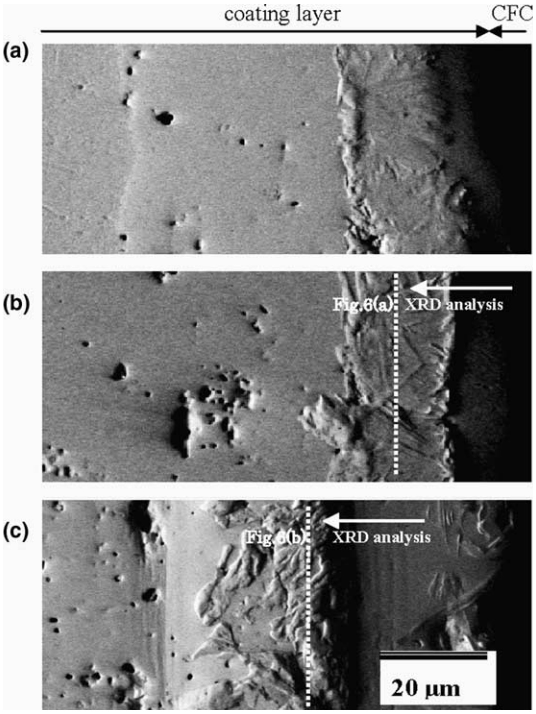

Fig. 5. Magnified backscattered electron (shadow) images near joint interface annealed for 3.6 ks at 1600 °C (a), 1.8 ks at 1800 °C (b) and 1.8 ks at 2000 °C (c).

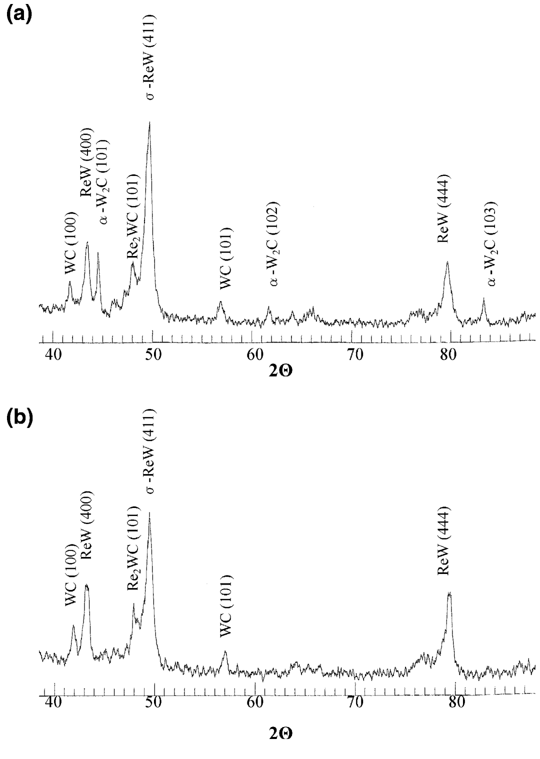

Fig. 6. X-ray diffraction analysis near joint interface annealed for 1.8 ks at 1800 °C (a), 1.8 ks at 2000 °C (b).

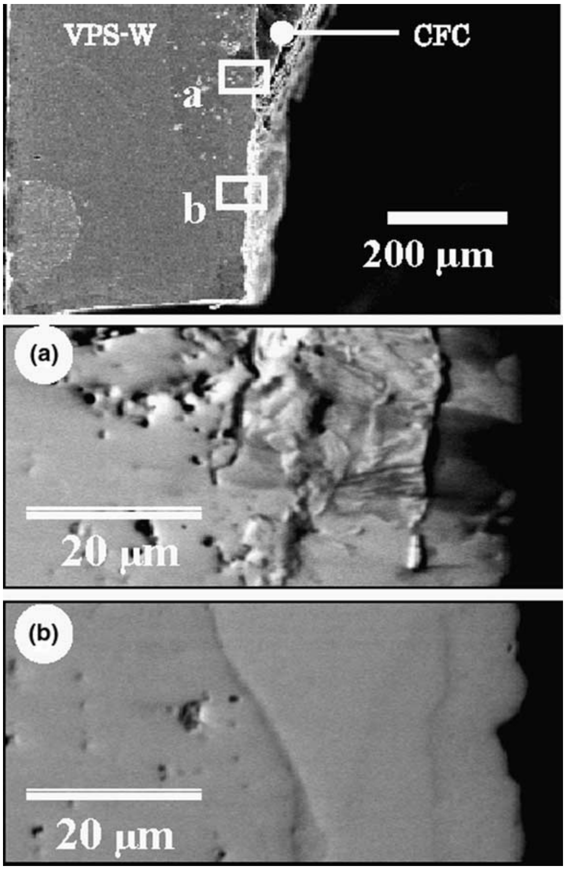

Fig. 7. Backscattered electron (shadow) images of the cross-section annealed for 3.54 ks at 1800 °C with CFC substrate (a), without CFC substrate (b).

carbide layer proceeded by solid-state diffusion of C atoms in the tungsten carbide layer according to a parabolic law $X^2 = kt$, with $k = 6.80 \times 10^{-8}$ $cm^2\,s^{-1}$.

3.3. Diffusion barrier at the joint interface

Fig. 5(a)–(c) shows magnified backscattered electron (shadow) images of the joint interface of the polished cross-section after annealing for 3.6 ks at 1600 °C (a), 1.8 ks at 1800 °C (b) and 1.8 ks at 2000 °C (c). At the joint interface of the samples having the logarithmic law, there is a layer which has hard dendrite structures. It was confirmed from the results of XRD, as shown in Fig. 6(a), that the layer is a compound of ReW, WC and W_2C. At the joint interface annealed for 1.8 ks at 2000 °C, the layer which has the dendrite structures was broken. As shown in Fig. 6(b), the composition of this broken layer was confirmed from a XRD analysis, that the broken layer consists of ReW and WC. The W_2C was not observed in this layer. That is to say, this constituent W_2C change into WC by absorbing C. To identify the chemical composition of the dendrite strictures, annealing for 3.54 ks at 1800 °C was carried out after removing from the CFC substrate. As shown in Fig. 7, the dendrite structures were not formed in the area of the multilayer without CFC substrate. This result indicates that the dendrite structures were made of tungsten carbide.

The carbon diffusivity in a grain of tungsten carbide is very low (2.25×10^{-15} $cm^2\,s^{-1}$ at 2000 °C), but that along the grain-boundary is much higher (5.10×10^{-5} $cm^2\,s^{-1}$ at 2000 °C) [8]. The present results indicate that the rapid formation of the tungsten carbide layer was caused by the fast diffusion of carbon along the grain-boundary.

4. Conclusions

From the electron beam heating tests of VPS-tungsten coated CFC, the following conclusions were obtained.

After the heat load test for 3.6 ks at 1400 °C, tungsten–rhenium multilayer at the joint interface of the coating was observed clearly. At the temperatures above 1600 °C, however, the multilayer was disappeared and a tungsten carbide layer was formed at the joint interface of the VPS-tungsten coating layer. At the temperatures below 1800 °C, the thickness of this layer logarithmically increased with increasing its annealing time. At 2000 °C, the growth of the tungsten carbide layer was proportional to the square root of annealing time. These results indicate that the diffusion barrier for carbon is not expected to suppress the carbide formation at the joint interface of the VPS-tungsten coating above 1600 °C.

Acknowledgements

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References

[1] N. Yoshida, J. Nucl. Mater. 266–269 (1999) 197.
[2] T. Tanabe, M. Wada, T. Ohgo, V. Philipps, M. Rubel, A. Huber, J. Von Seggern, K. Ohya, A. Pospieszczyk, B. Schweer, J. Nucl. Mater. 283–287 (2000) 1128.
[3] A. Pospieszczyk, T. Tanabe, V. Philipps, G. Sergienko, T. Ohgo, K. Kondo, M. Wada, M. Rubel, W. Biel, A. Huber, A. Kirschner, J. Rapp, N. Noda, J. Nucl. Mater. 290–293 (2001) 947.
[4] K. Tokunaga, N. Yoshida, N. Noda, Y. Kubota, S. Inagaki, R. Sakamoto, T. Sogabe, L. Plöchl, J. Nucl. Sci. Technol. 27 (4) (1990) 333.
[5] K. Tokunaga, T. Matsubara, Y. Miyamoto, Y. Takao, N. Yoshida, N. Noda, Y. Kubota, T. Sogabe, T. Kato, L. Plöchl, J. Nucl. Mater. 283–287 (2000) 1121.

[6] S. Deschka, C. Garcia-Rosales, W. Hohenauer, R. Duwe, E. Gauthier, J. Linke, M. Lochter, W. Mallener, L. Plöchl, P. Rodhammer, A. Salito, J. Nucl. Mater. 233–237 (1996) 945.

[7] K. Tokunaga, K. Matsumoto, Y. Miyamoto, N. Yoshida, J. Nucl. Mater. 212–215 (1994) 1323.

[8] C.P. Buhsmer, P.H. Crayton, J. Mater. Sci. 6 (1971) 981.