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Effect of heat-treatment at different temperatures on the phase and morphology of the surface of W-coated C/C composites

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ABSTRACT

W-coated carbon/carbon composites have been considered as an attractive plasma facing material for ITER. W coatings were prepared on carbon/carbon substrates by double glow plasma. W-coated carbon/carbon substrates were heat-treated in a vacuum furnace at 1000, 1100, 1200, 1300 and 1400 °C for 1 h. The coatings were examined by X-ray diffraction for phase identification. The microstructure was observed by scanning electron microscopy. The chemical composition was analyzed by energy dispersive X-ray spectroscopy. The Vickers hardness was measured with a microhardness tester. The results indicated that the critical temperature for generating WC was 1200 °C. When the coatings were heat-treated below 1200 °C, the diffusion of W and C played a dominant role. W grains in 1100 and 1200 °C heat-treated samples presented a diffusion-induced rearrangement around the carbon fibers or the pores on the surface of C/C substrate. The amount of W and the hardness of the heat-treated coatings were reduced as the temperature increased. However, the reaction of W and C played a dominant role above 1200 °C. The amount of WC and the hardness of the heat-treated coatings were greatly increased as the temperature increased.

1. Introduction

Because of its low sputtering yield and good thermal properties, W is presently regarded as an excellent candidate material for diverter armor tiles of ITER. As a result, the interactions between W and plasma had been intensively studied [1]. Disadvantages of W as a plasma facing material for the ITER are its heavy weight and poor workability. To overcome these disadvantages, light carbon materials coated with W have been evaluated and have shown good heat load resistance in present plasma confinement devices such as the Tokamak Experiment for Technology Oriented Research (TEXTOR) and Axially Symmetric Divertor Experiment (ASDEX)-Upgrade [2–5]. Thick W coatings on C/C composites and isotropic fine grain graphite were successfully produced and their good thermal and adhesion properties have been confirmed by high heat flux tests [6,7]. In these experiments, W concentration in the main plasma remained below 2×10^{-5}, which was below the tolerable maximum impurity concentration in ITER ignited plasma [4]. However, the main impurity was still carbon due to the interactions between the first wall and other plasma facing components made of graphite or carbon based materials [8]. W coating prepared by vacuum plasma spray and physical vapor deposition always presented some porosity and micro-cracks where carbon element in C/C composites could significantly sputter out and the W armors could be quickly covered by re-deposited carbon. DGP (double-glow plasma), an evolution of both plasma nitriding and sputtering techniques, could apply almost all solid metallic elements to realize surface alloying of the substrates. Continuous, dense and adhesive metallic coating could be obtained on metal or nonmetal substrate by DGP [9,10]. The deposition rate of the coating prepared by DGP was quicker than by physical vapor deposition. The coating obtained by DGP was denser than by plasma spray [11–13]. Investigating the evolution of W coating on the C/C composites at high temperature was very important to modify the W-coated C/C composites. In this study, W-coated C/C composites (W coating ~3 μm) were heat-treated at 1000, 1100, 1200, 1300 and 1400 °C. The phase and microstructure of the surface of the heat-treated coating were investigated.

2. Experimental procedure

W coatings were prepared on the surface of C/C substrates (porosity 4–6%; density 1.85–1.90 g/cm^3) by DGP in a vacuum sputtering chamber. There were three electrodes in the vacuum chamber: one anode and two negatively charged members, the cathode where the work piece was located, and the source electrode where the desired alloying elements were placed. In this experiment, a pure W plate was used as the source electrode material for supplying alloying element. C/C composites were used as the substrate material. Both the cathode and the source electrode were surrounded by the glow discharges when the power was

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turned on. The first glow discharge heated the substrate to a high temperature while the second glow struck the source electrode. The desired alloying elements were sputtered by the second glow from the source electrode, traveling toward the substrate. Subsequently the alloying elements deposited onto the surface of the C/C substrate [9]. The cathode power was always turned on first and one glow was discharged to heat and clean the C/C substrate, which was beneficial to the deposition. This process was called as 'cathode heating-cleaning process', and then the source electrode power was turned on. In this experiment, the cathode heating-cleaning process parameters were as follows: cathode voltage 350 V; working pressure 50 Pa; holding time 1.5 h. Deposition process parameters were as followed: source voltage 850 V; cathode voltage 550 V; working pressure 50 Pa; holding time 0.5 h; distance between the target and substrate 16 mm.

The W-coated C/C substrates were heat-treated at 1000, 1100, 1200, 1300 and 1400 °C for 1 h in a vacuum furnace using graphite as the heating element and crucible. The heating-up time was 4 h. The pressure of the vacuum furnace was retained at 50 Pa by inputting 500 ml/min argon flux.

The coating was examined by X-ray diffraction (XRD, Rigaku D/Max-B) for phase identification using Ni-filtered CuK_a radiation at a scanning rate of 4°/min. The microstructure was observed by scanning electron microscopy (SEM, JEOL, JSM-6360). The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDS, LINK-860). The Vickers hardness was measured with a microhardness tester (HXS-1000).

3. Results and discussion

Fig. 1 shows the XRD patterns of the surfaces of the as-prepared coating and the heat-treated coatings. The θ–2θ scan data exhibited strong 2θ peaks at 40.265°, 58.276°, 73.198°, corresponding to the (1 1 0), (2 0 0), (2 1 1) peaks compared with the standard X-ray powder diffraction pattern (JCPDS card, No: 4-806). The XRD pattern revealed that the as-prepared W coating had a polycrystalline structure and a preferential growth orientation perpendicular to (2 1 1) crystal plane.

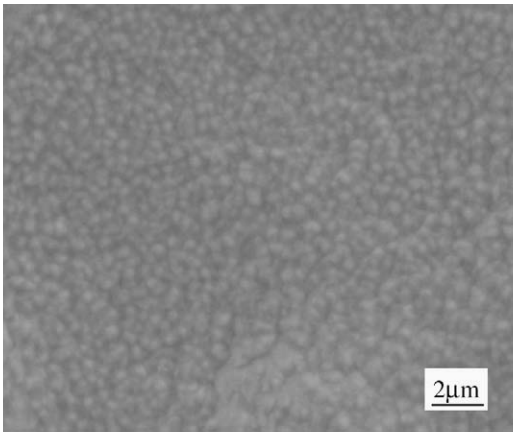


Fig. 2. SEM micrograph of the surface of the as-prepared coating.

Fig. 2 shows the SEM micrograph of the surface of the as-prepared coating. It was found that the surface of the C/C substrate was covered by a large amount of close-packed W particles. Because the coating was too thin to completely obstruct the X-ray, a trace amount of the elemental C was observed in the XRD (see Fig. 1(a)). The crystal plane of the original W coating had changed after 1000 °C heat-treatment. The XRD peak of the (1 1 0) crystal plane became the strongest, which accorded with the standard X-ray powder diffraction pattern (JCPDS card, No: 4-806). The intensities of the diffraction peaks of the elemental W were increased and the width of the half-height of the peak of the elemental W was reduced after 1000 °C heat-treatment. It indicated that the W grains grew up and the original growth orientation of the W grains also had changed [14,15]. Strong C and W peaks were synchronously present in the 1000 and 1100 °C heat-treated coatings. WC peaks appeared in the 1200, 1300 and 1400 °C heat-treated coatings. According to the reaction thermodynamics of W and C [16], W can react with C when the temperature exceeds 1200 °C and the reaction was more drastic as the temperature increased. The diffraction peak of the (0 0 1) crystal plane of WC compound

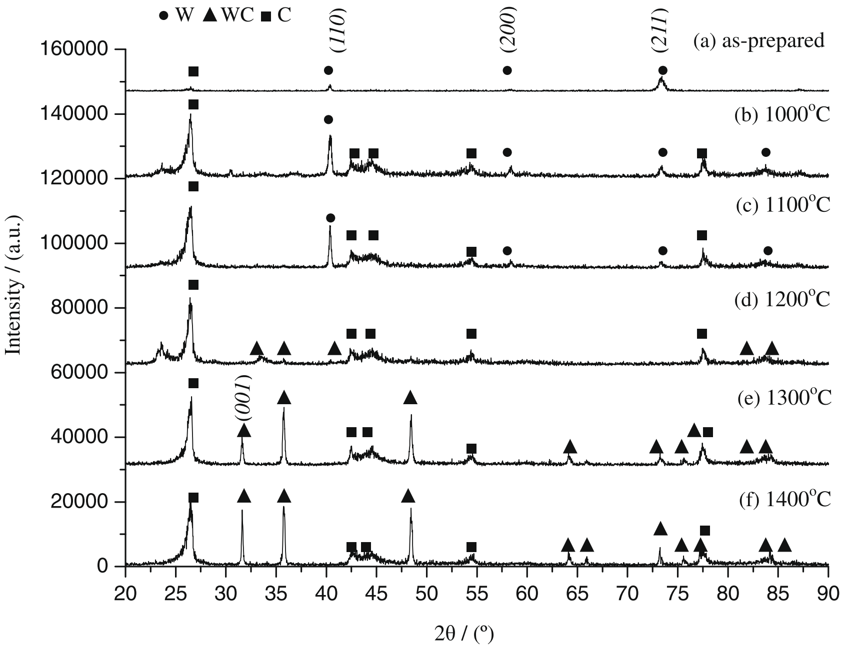


Fig. 1. XRD patterns of the surfaces of the as-prepared coating and the heat-treated coatings.

was strongly enhanced after 1400 °C heat-treatment. It indicated that the WC grains had been completely crystallized.

Fig. 3 shows the SEM micrographs of the surface of the 1000 °C heat-treated coating. The surface was covered by a lot of discontinuously recrystallized W circles, which could result from the microstructure of the C/C composites and the shrink of the coating. Fig. 4 displays the SEM micrograph of a fracture surface of the C/C composites. It was found that the carbon fiber was surrounded by a circle pyrolytic carbon which had a multilayer microstructure. Fig. 5 shows a schematic of the cross-section of the coating. The surface of the discontinuous pyrolytic carbon was covered by a continuous W film in the as-prepared coating. After heat-treatment, the coating was torn out from the gap and became discontinuous. The centers of the W circles could be the carbon fiber filaments.

Fig. 6 shows the SEM micrographs of the surface of the 1100 °C heat-treated coating. Because the thermal diffusion of W element into C/C substrate was enhanced, the amount of C on the surface was significantly reduced (see Fig. 1(c)). It was also found that W element tended to aggregate in the pores on the C/C substrate or around carbon fiber.

Fig. 7 shows the SEM micrographs of the surface of the 1200 °C heat-treated coating. Although the surface morphology of the 1200 °C heat-treated coating was not different from the 1100 °C heat-treated coating, the W peaks disappeared and WC peaks appeared (see Fig. 1(d)). The results indicated that the critical reaction temperature between W and C was 1200 °C. C/C composites were composed of the carbon fiber, pyrolytic carbon matrix with a lamination microstructure, and 4–6 vol.% pores resulting from the preparation method of chemical vapor infiltration [17,18]. In general, the atoms on a void surface diffuse from high chemical potential regions to low chemical potential region, which causes the void to change its shape or drift along the metal line. The diffusion driving force relates to the chemical potential. Because the chemical potential of the convex surface is higher than that of concave, the pores have good capability of capturing the elemental W [19]. The laminative pyrolytic carbon had so good adsorbability to the elemental W, that W element was prone to aggregate around the carbon fiber [20].

Fig. 8 shows SEM micrographs of the surface of the 1300 °C heat-treated coating. Discontinuous white areas were inlaid in black areas of the heat-treated coating. The white area was composed of a large of white particles. The former investigation showed the composition of the black area was mainly the elemental C and the composition of the white particle was C and W [21]. According to XRD and EDS patterns, the white particles were proved to be the WC grains in the 1200, 1300 and 1400 °C heat-treated coatings.

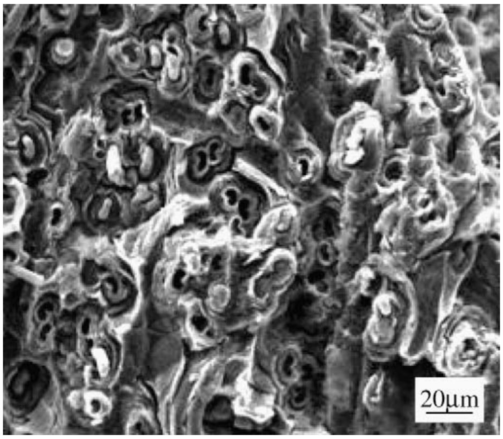
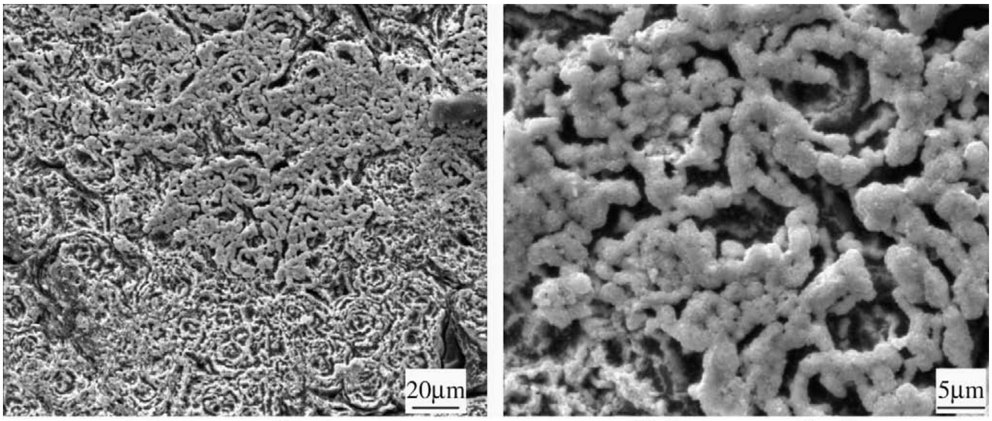


Fig. 4. SEM micrograph of the fracture surface of C/C composites.

Fig. 9 shows the SEM micrographs of the surface of the 1400 °C heat-treated coating. The heat-treated coating was composed of a large of the columnar WC grains. The SEM and XRD indicated that the amount of WC gradually increased from 1200 to 1400 °C. WC grains had been completely crystallized after 1400 °C heat-treatment. Because all of the heating-up times were 4 h, the heating rate of the 1400 °C heat-treatment was the fastest in the four heat-treatment coating. The elemental W could have no enough time to diffuse into C/C substrate. The reaction of W and C at 1400 °C was more drastic than the diffusion, which played a dominant role, and resulted in a mass of WC remained on the surface of the coating.

Fig. 10 displays the surface Vickers hardness chart of the as-prepared and the heat-treated coatings. The loading force was 2 N and the loading time was 15 s. The surface hardness of the coatings decreased as the heat-treatment temperature increased below 1200 °C. The surface hardness presented ascending trend above 1200 °C. The surface hardness of 1400 °C heat-treated coating was the highest. Because the thermal diffusion of W element into C/C substrate was enhanced as temperature increased below 1200 °C, the amount of C on the heat-treated coating was reduced. The reduction of W content led to the reduction of the surface hardness of the heat-treated coating. When the temperature reached 1200 °C, WC with a higher hardness than W was generated. The amount of WC on the heat-treated coating increased as the heat-treatment temperature increased, as a result, the surface hardness of the heat-treated coating greatly increased.



(a) Low magnification (b) Large magnification

Fig. 3. SEM micrographs of the surface of the 1000 °C heat-treated coating.

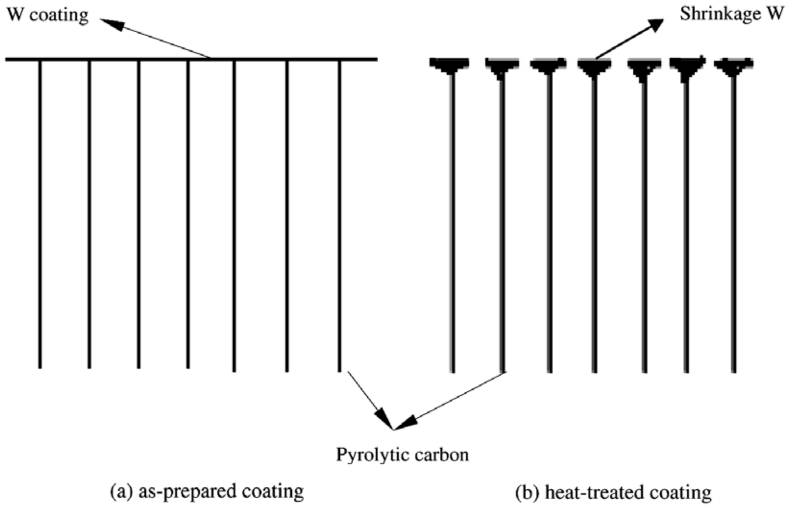
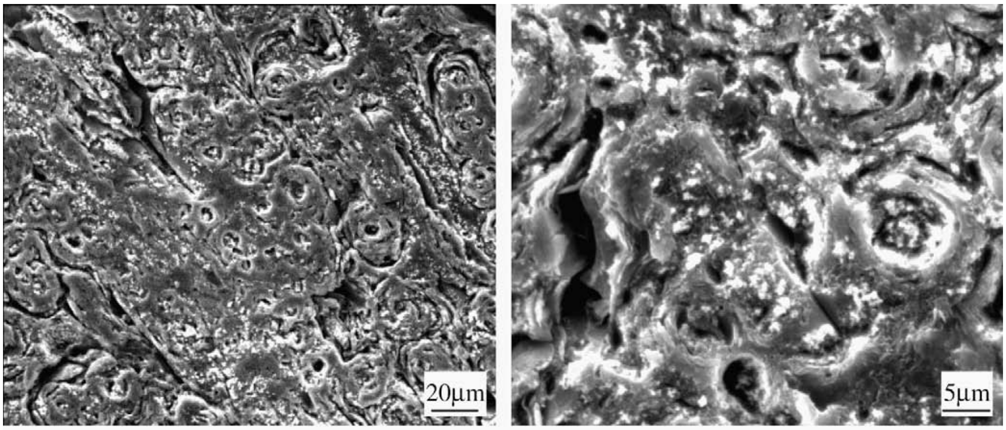
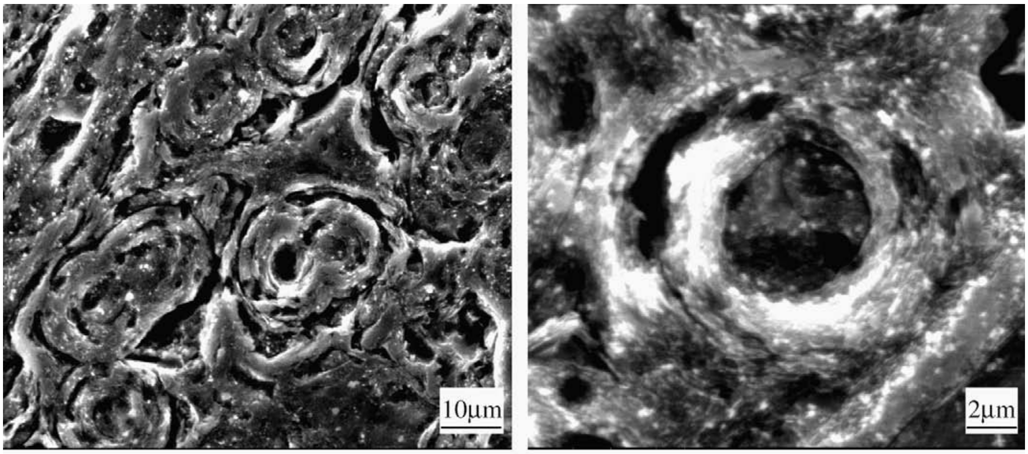


Fig. 5. Schematic of the cross-section of the coating.



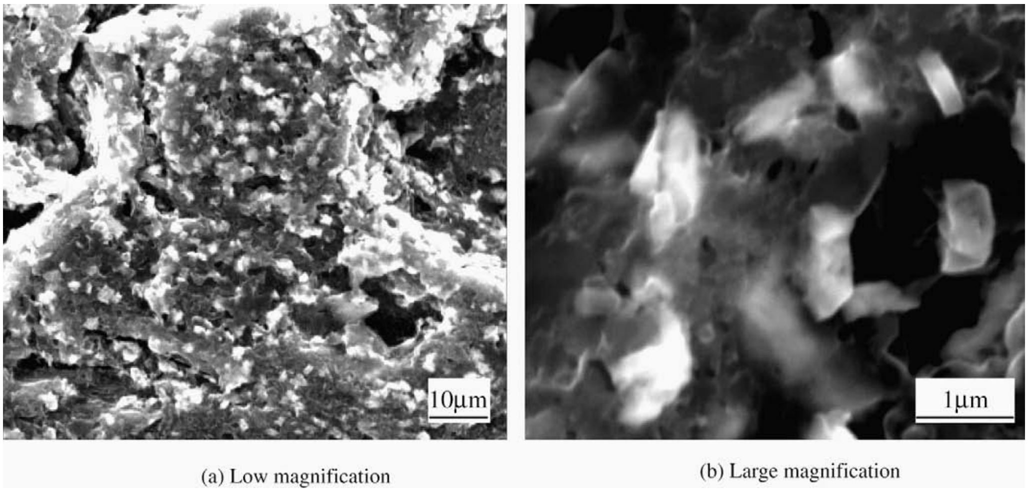
(a) Low magnification (b) Large magnification

Fig. 6. SEM micrographs of the surface of the 1100 °C heat-treated coating.



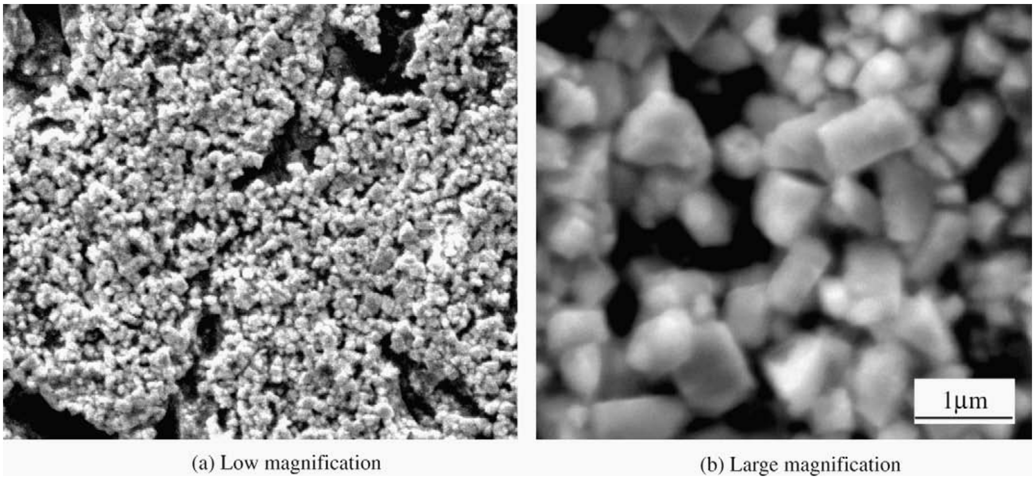
(a) Low magnification (b) Large magnification

Fig. 7. SEM micrographs of the surface of the 1200 °C heat-treated coating.



(a) Low magnification (b) Large magnification

Fig. 8. SEM micrographs of the surface of the 1300 °C heat-treated coating.



(a) Low magnification (b) Large magnification

Fig. 9. SEM micrographs of the surface of the 1400 °C heat-treated coating.

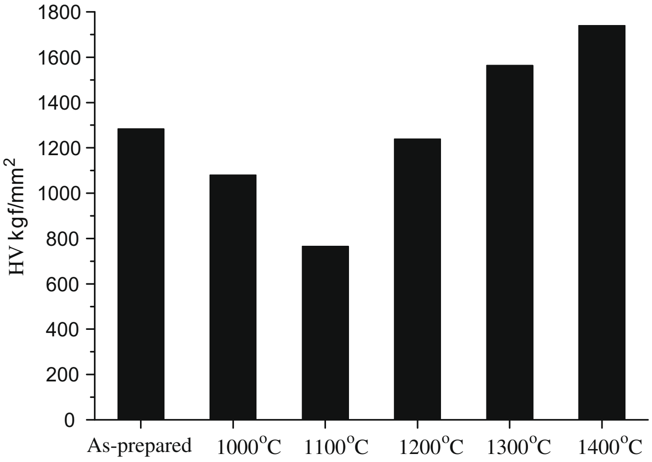


Fig. 10. Surface microhardness chart of the as-prepared and the heat-treated coatings.

The present results could be useful to support the W-coated C/C composites by DGP technology as facing material of ITER. In general, W had a high diffusion rate in carbon material, which could limit the service time of the W coating. However, the high temperature and heating rate resulted from the plasma would increase the reaction and inhibit the diffusion between W and C/C substrate. When rhenium is used as the diffusion barrier layers, the diffusion of W coating is delayed up to 1600 °C [7]. However, 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 [6].

4. Conclusions

Heat-treatment had dramatic effect on the microstructure and the phase composition of the surface of W-coated carbon/carbon composites deposited by double glow plasma. Heat-treatment condition of W-coated carbon/carbon composites was intentionally applied to the coating before the service for making a reaction layer.

When heat-treatment below 1200 °C, the diffusion between W and C played a dominant role. However, above 1200 °C, the reaction between W and C was more drastic than the diffusion.

Below 1200 °C, the amount of C in the heat-treated coating was reduced as the heat-treatment temperature increased, which led to the reduction of the surface hardness. Above 1200 °C, the amount of WC in the heat-treated coating was greatly increased as the heat-treatment temperature increased, which led to the increase of surface hardness.

Below 1200 °C, W grains presented a diffusion-induced rearrangement around carbon fibers or in the pores on the C/C surface. Above 1200 °C, the columnar WC grains maturely formed as heat-treatment temperature increased.

Acknowledgement

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