



Surface analysis of VPS-W coatings boronized by an ICRF discharge in HT-7

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ARTICLE INFO

Article history:

Available online 24 December 2010

ABSTRACT

To understand the surface compositions and the hydrogen isotope behavior in boronized Vacuum plasma spraying (VPS)-W, the boron coating has been achieved by means of Ion Cyclotron Radio Frequency (ICRF) boronization using carborane ($C_2B_{10}H_{12}$) powder as the precursor material in HT-7. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to observe the morphology of the VPS-W and boronized W surfaces. The X-ray Photoelectron Spectroscopy (XPS) of W-4f, O-1s, C-1s and B-1s on the VPS-W sample before and after boronization and after plasma exposure have been measured. The B–B and B–C bonds were observed after boronization treatment for VPS-W. Thermal Desorption Spectroscopy (TDS) experiments were also carried out to investigate the thermal desorption behavior of D implanted into the samples. After HT-7 plasma exposure, the desorption spectrum had a low temperature peak associated with trapping in intrinsic defects in polycrystalline W and a high temperature peak associated with B–O–D and B–C–D bonds.

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1. Introduction

Ion Cyclotron Radio Frequency (ICRF) wall-conditioning techniques have been routinely used in the HT-7 superconducting tokamak during the past ten years [1–3] to develop the physics and technologies for quasi-steady state plasma operation. The wall coating was achieved by means of ICRF boronization using carborane ($C_2B_{10}H_{12}$) [4] powder as the boronization material. This technique has been demonstrated to be very effective for impurity reduction of the plasma discharge. However, there is a lack of detailed surface analysis to the boron coatings. In addition, the large amount of hydrogen contained in the fresh boron film caused a serious recycling problem calling for thorough understanding of the behavior of hydrogen isotope trapped in the coatings.

Tungsten (W) and its alloys have been considered as candidate plasma-facing materials (PFM) for ITER, future DEMO reactors [5], and the Experimental Advanced Superconducting Tokamak (EAST), attributed to their favorable properties, e.g., low sputtering yield, no chemical erosion, low tritium retention, good thermo-mechanical properties. Vacuum plasma spraying (VPS) is very useful in preparing for thick W coatings due to its high coating rate and possibility of in-field repairing. In our previous work, W coatings on Cu have been developed by VPS adopting a Cu/W gradient interlayer. Then VPS-W/Cu PFCs with built-in cooling channels were prepared and mounted into the HT-7 acting as a directly-cooled movable limiter served as a nice test bench for materials evaluation [6,7]. The W/Cu PFCs may be tested directly on the EAST in 2–3 years,

and gradual deployment may be expected in 3–5 years. It is very important to get the detailed information of the surface compositions and to understand the hydrogen isotope behavior in boronized VPS-W. The purpose of this work is to provide some physical basis for the applications of W coatings and boronizations in the EAST tokamak.

2. Experiments

The preparation of VPS-W coatings on Cu and physical experiments of VPS-W/Cu movable limiter in HT-7 have been reported in Refs. [6,7]. ICRF boronization in HT-7 was accomplished using carborane ($C_2B_{10}H_{12}$) powder in this work. In order to obtain the best boron film coating results, a set of optimized ICRF conditioning parameters were chosen: the vacuum vessel and liner were baked to 80–120 °C and 150–180 °C, respectively and the temperature of the VPS-W sample was ~150 °C. The pressure was 0.3 Pa with a mixture of helium to carborane of 1:1. A pulsed ICRF power of 15–30 kW (30 MHz) was coupled to the plasma with power on for 2.0 s and off for 1.0 s. The toroidal magnetic field was 1.8 T.

The samples in this work have been divided into three groups, namely A, B and C: sample A is the pure VPS-W as reference before boronization; sample B is the boron coated VPS-W; sample C is the sample B with plasma exposure in HT-7. HT-7 is a medium-sized superconducting tokamak with limiter configuration and its major and minor radius are $R = 1220$ mm and $a = 270$ mm, respectively. The minor radius a is determined by the fixed graphite limiters [8]. Sample C was exposed to an Ohmic deuterium plasma (shot #102,702) coupled with lower hybrid current drive (LHCD) and

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ICRF power with plasma current $I_P \sim 126$ kA, line average density $\sim 2.2 \times 10^{19} \text{ m}^{-3}$, central electron temperature ~ 900 eV, and pulse duration of 0.92 s.

Surface morphology was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS, ESCA 1600, ULVAC PHI Inc.) were performed to analyze the elementary composition and assess the level of impurities (oxygen and carbon). The Al $K\alpha$ (1486.7 eV) was used as an X-ray source. The pressure in the chamber was maintained at 10^{-7} – 10^{-8} Pa. To investigate the thermal desorption behavior of D_2 implanted into the samples, Thermal Desorption Spectroscopy (TDS) experiments were carried out after the D_2^+ implantation. For samples A and B, the experimental procedure was as follows: first, the sample was preheated from R.T. to 723 K to remove the impurity in the sample with the heating rate of 30 K min^{-1} . The set temperature would be kept for 10 min under a pressure $\sim 10^{-6}$ Pa. Then the sample was cooled down to R.T. Secondly $1.0 \text{ keV } D_2^+$ ion implantation was performed at R.T. under a pressure of 10^{-6} Pa. The flux was $1.0 \times 10^{18} \text{ D}^+ \text{ m}^{-2} \text{ s}^{-1}$ and the implantation time was 10,000 s, which resulted in a total fluence of $1.0 \times 10^{22} \text{ D}^+ \text{ m}^{-2}$. Then the TDS measurement was performed from R.T. to 993 K with a rating of 30 K min^{-1} for samples A–C.

3. Results and discussion

Fig. 1 shows the surface SEM and AFM images of samples A–C. After ICRF boronization processing, relatively smooth and uniform films were formed on the VPS-W as shown in Fig. 1.B. After D plasma exposure, the micro etching holes have emerged on the surface and part of the boron film has peeled off from the surface. From the AFM images we can see the difference of the roughness after different processing. Thickness of the boron film for the sample B was measured by AFM, which was given to the value of about 160 nm.

Following the surface morphology observation, XPS measurements were performed for samples A–C. From Fig. 2a, it can be seen that the two binding energies for W metal, namely 31.5 eV and 34 eV, cannot be observed after boronization indicating the boron coating formed on the surface. Binding energy ranged from 35.5 eV to 36.34 eV for WO_3 is also found for Sample A. After plasma

exposure in HT-7, binding energies for W emerged again, in consistent with the SEM observation that the boron film is partially removed from the surface of VPS-W. The fact that cohesion between the boron film and VPS-W was poor, indicated a challenge to develop new boronization technique in order to meet the needs in the near future when W will be used in EAST as divertor and first-wall materials.

In B-1s spectra, it has been known that the B–B, B–C and B–O bonds are located at the peak energies of 187.8 eV, 189.0 eV and 190 eV, respectively [9,10]. The above binding energies were observed for sample B after boronization processing treatment for sample A. After exposure to D plasma discharge, the peak energies of B-1s XPS spectra were shifted toward higher energy side indicating that D were bound to B [10–13].

Fig. 2c shows O-1s spectra of samples A–C. The O-1s binding energy for VPS-W is located at 531 eV, denoting the oxide in transitional metal [14]. After boronization treatment, the binding energy was shifted to 532.8 eV, denoting the B_2O_3 bond incorporated into boron film. After D plasma discharge was performed, the binding energy of spectrum for O-1s was similar to sample A. The binding energy was located in the range from 531.2 to 532.2 eV, denoting the mixture of C=O bond and WOOD oxyhydroxide.

Fig. 2d shows C-1s spectra of samples A–C. The C impurity was incorporated into the VPS-W surface after boronization treatment. The C-1s binding energy of 285 eV for C–C bond was clearly observed, corresponding to the chemical state of the carborane ($C_2B_{10}H_{12}$) powder used as gas source in boronization processing. The binding energy of 284.9 eV denoted the graphite C formed on the surface of sample C. The binding energy of 284.5 eV denoted the C–B (sp²) bonding formed on the surface of sample B and also found in sample B are C–C (sp²) 284.9 eV and other C bonds relative to the impurities existing in HT-7 Tokamaks [15,16]. After D plasma exposure, the peak shift of C-1s toward the lower energy side was observed and the FWHM value of C-1s peak increased as shown in Fig. 2d, which is similar to the O-1s as shown in Fig. 2c. The peak areas of C-1s and O-1s mean the relative content of C and O. The dramatic increase of the peak area after plasma discharge was related to plasma contamination including C and O and eventually the C and O were incorporated on the surface.

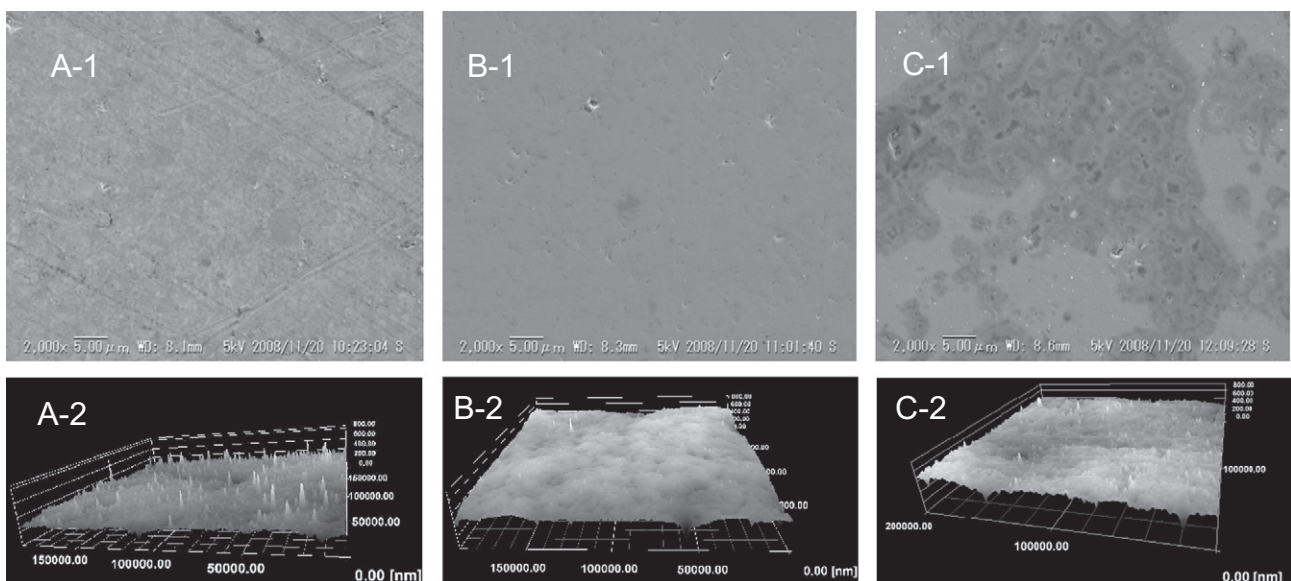


Fig. 1. Surface SEM and AFM images of samples A–C. Sample A is the pure VPS-W as reference before boronization. Sample B is the boron coated VPS-W. Sample C is the sample B with D plasma exposure in HT-7.

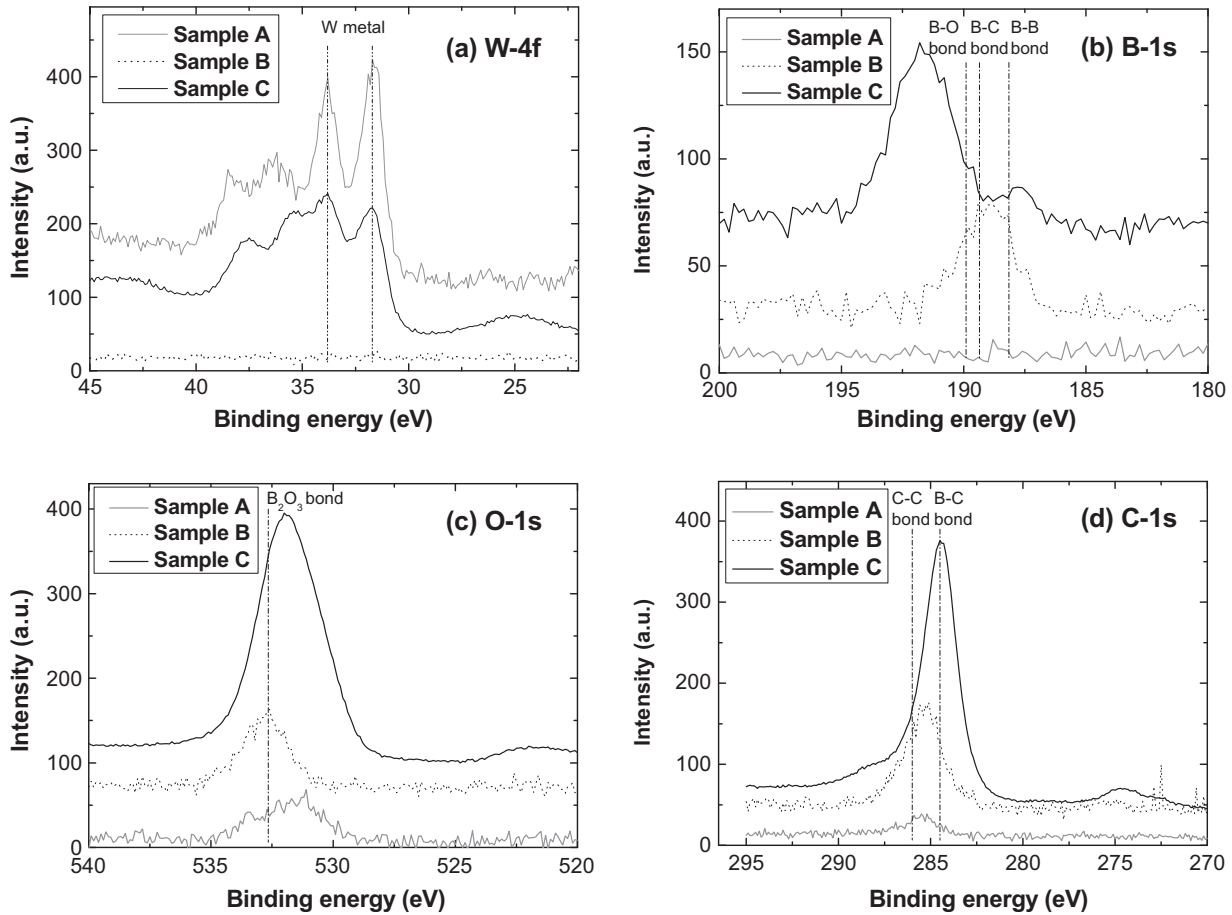


Fig. 2. XPS spectra of samples A–C: (a) W-4f, (b) B-1s, (c) O-1s and (d) C-1s.

To investigate the chemical states of deuterium trapped in the samples and elucidate its desorption behavior from the surface, TDS experiments have been performed. Fig. 3 shows the TDS spectra of D_2^+ desorbed from samples A–C. TDS for sample A, which consisted of polycrystalline W (PCW), has a low temperature peak with a maximum about 450 K, which can be associated with D trapping in intrinsic defects (dislocations, grain boundaries, some impurities) always present in PCW [17]. The D_2 TDS spectrum for boronized W, namely sample B, and peak analysis using Gaussian distribution function are also shown in Fig. 3. From the peak anal-

ysis, the spectrum could be divided into four desorption stages at the peak temperature of 500 K, 630 K, 837 K and 932 K, namely Peak 1, Peak 2, Peak 3 and Peak 4 respectively. Comparing the spectra with the results in previous study in Refs. [11,18,19], where pure boron coating films and carbon-contained boron films were prepared by plasma chemical vapor deposition, it can be deduced that Peaks 1 and 2 correspond to the desorption stages of deuterium bound to boron with forming B–D–B bridge bond and B–D terminal bond respectively. Peaks 3 and 4 were thought to be corresponded to the desorption of D trapped by O and C [10]: Peak 3 of TDS spectrum was attributed to B–O–D bond and Peak 4 corresponded to the desorption stage of D trapped by C with forming B–C–D bond, which is consistent with the XPS results that B–O and B–C bonds were observed for B-1s with the shift of peak energy after plasma discharge and simultaneously B–O for O-1s and B–C for C-1s were observed respectively. Carbon incorporated into the boron coating originated from: $C_2B_{10}H_{12}$ (gas source) in boronization processing and inherent C impurity inside the vacuum vessel of HT-7 Tokamak which adopting carbon based materials as PFM. After plasma exposure, the desorption spectrum for sample C has showed the characteristic of mixture of samples A and B: low temperature peak associated with trapping in intrinsic defects in PCW and high temperature peak associated with B–O–D and B–C–D bonds.

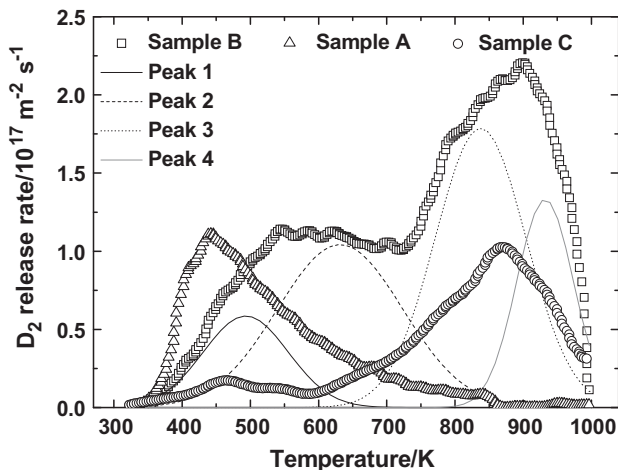


Fig. 3. TDS spectra of samples A–C.

4. Conclusions

To understand the surface compositions and the hydrogen isotope behavior in boronized VPS-W, the coating has been achieved

by means of ICRF boronization using carborane ($C_2B_{10}H_{12}$) powder as the boronization material in HT-7. SEM and AFM were used to observe the surface morphology of the VPS-W and boronized W surface. After ICRF boronization processing, relatively smooth and uniform films were formed on the VPS-W surface. After the D plasma exposure, the micro etching holes have emerged on the surface.

The XPS measurement was performed to evaluate the elementary composition characterization and assess the level of impurities. The binding energies for W metal, namely 31.5 eV and 34 eV, cannot be observed after boronization treatment. In B-1s spectra, the B–B and B–C bonds (peak energies located at 187.8 eV and 189.0 eV, respectively) were observed after boronization processing treatment for VPS-W.

TDS for VPS-W has a low temperature peak with a maximum about 450 K, which can be associated with trapping in intrinsic defects always present in PCW. For the boronized W, two broad desorption peaks of D_2 were observed: The first peak from about 500 K to 650 K at low temperature range and the second one about 830 K to 950 K at high temperature range corresponding to the desorption of D bound to B and the bridge bonds B–O–D and B–C–D due to O and C incorporation into the boron film respectively.

Acknowledgements

This work was supported partially by the National Natural Science Foundation of China under Contract Nos. 10905070, 10875148 and 10728510, the Knowledge Innovation Program of

the Chinese Academy of Sciences, National Magnetic Confinement Fusion Program with Grant Nos. 2009GB106005, 2010GB109004 and the JSPS-CAS Core-University Program in the field of Plasma and Nuclear Fusion. The XPS and TDS measurements were done at the Center for Instrumental Analysis at Shizuoka University.

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