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Solid state reaction between tungsten and amorphous carbon

Yuji Hatano [a,*], Miyuki Takamori [a], Kenji Matsuda [b], Susumu Ikeno [b], Katsuhiko Fujii [c], Kuniaki Watanabe [a]

[a] *Hydrogen Isotope Research Center, Toyama University, Gofuku 3190, Toyama 930-8555, Japan*
[b] *Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Gofuku 3190, Toyama 930-8555, Japan*
[c] *Institute of Nuclear Safety System, 64 Sata. Mihamacho, Mikata-gun, Fukui 919-1205, Japan*

Abstract

The solid state reaction between tungsten and amorphous carbon was studied at 973, 1073 and 1173 K. An amorphous carbon film was deposited onto a tungsten sheet by vacuum evaporation. The specimens thus prepared were heated at given temperatures, and the time dependence of carbide growth was examined by means of X-ray diffraction. No carbide appeared at 973 K within 240 min. On the other hand, the peaks of W_2C appeared at 1073 and 1173 K after an induction period, although W_2C is not thermodynamically stable at these temperatures. The intensities of W_2C peaks increased with elapse of time and then decreased owing to the decomposition of W_2C. No diffraction peaks from WC were detected at both temperatures. It was concluded that the rates of nucleation and growth of W_2C are significantly higher than those of WC at these temperatures.

1. Introduction

Low-*Z* materials such as carbon and beryllium have been widely used for plasma facing components in magnetic confinement fusion devices to reduce radiation loss from the plasma [1,2]. On the other hand, high-*Z* materials such as tungsten and molybdenum have better durability against heat loads and particle bombardments [3]. Hence, it is now common to use two or more plasma facing materials being complementary to each other. Under such conditions, sputtering and evaporation of one of the plasma-facing materials result in deposition onto other coexisting materials and modify the surface properties. Fuel recycling and inventory become complicated through such surface modification. An understanding of the properties of deposited layers is necessary for the selection of the plasma facing materials in the next generation fusion devices.

The present authors have examined the properties of hydrogen containing carbon (C(H)) film deposited onto tungsten sheet by rf discharge in methane and ethylene as a model system to simulate co-deposited layers on the surfaces of tungsten divertors [4]. Namely, the solid state reaction between the C(H) film and the substrate has been examined at a temperature range from room temperature to 1273 K by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy. Carbon started to react with tungsten at ≈900 K to form W_2C and a large amount of hydrogen was released through this reaction. These observations suggest that the chemical states of carbon have a strong influence on the fuel recycling and inventory at tungsten divertors with carbon deposition. Luthin and Linsmeier [5,6] have also examined the reaction between a tungsten sheet and a thin carbon film without hydrogen by means of XPS. In contrast to our results, they observed not only W_2C but also WC. It is therefore interesting to examine the influence of the hydrogen presence on the reaction between carbon and tungsten. In these studies, however, the time dependence of the reaction was not examined although the reaction products can change

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[*] Corresponding author. Tel.: +81-76 445 6928; fax: +81-76 445 6931.

E-mail address: hatano@hrc.toyama-u.ac.jp (Y. Hatano).

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with time; a specimen was heated at a given temperature only for 10 min in our previous study [4] and for 30 min in the researches of Luthin and Linsmeier [5,6]. Hence, it is necessary to investigate the time dependence of reaction for both the C(H)/W and C/W systems.

From this viewpoint, the time dependence of reaction between tungsten and a carbon film without hydrogen was examined in the present study. An amorphous carbon film was deposited onto a tungsten sheet by vacuum evaporation. The specimens thus prepared were heated at 973, 1073 and 1173 K from 0.5 to 240 min, and the time dependence of carbide growth was examined by X-ray diffraction (XRD).

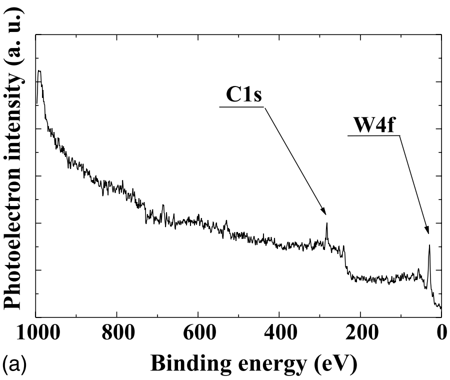
2. Experimental

A tungsten specimen of 10 × 10 × 0.3 mm^3 was cut from a sheet supplied by Nilaco (99.95 wt% purity). The surface of the specimen was polished with SiC abrasive papers and finished with 0.06 μm Al_2O_3 powder. A carbon film of ≈10 nm thickness was deposited onto the specimen surface with a conventional ohmic heating carbon evaporator evacuated with an oil-sealed rotary pump. The deposition rate was ≈5 nm min^{-1}. In order to examine the crystal structure, carbon was evaporated onto a tungsten mesh in the manner described above, and a film deposited on the edge of wire was examined with a transmission electron microscope (TEM). The chemical form of tungsten at the C/W interface was examined by XPS. In this case, a thin film (≈3 nm) was prepared by reducing the evaporation time.

The specimen with carbon film of ≈10 nm thickness was heated at 973, 1073 and 1173 K for 0.5–240 min in the vacuum system used for the thermal desorption experiments in the previous study [4]. The pressure of the residual gas was 1 × 10^{-5} Pa or lower, and the dominant residual gas was water vapor. After heat treatment, the specimen was taken out from the vacuum system and analyzed by means of XRD. The specimen was placed on a holder made of aluminum and analyzed in 2θ geometry over the range from 3° to 90° with Cu Kα radiation, where the incident angle of X-rays was adjusted to 1.5° to analyze the shallow region from the surface. The specimen heated at 1073 K for 70 min was analyzed by using a scanning Auger microscope (SAM) in order to examine a major chemical form of carbon and uniformity of the reaction.

3. Results and discussion

In the TEM analysis, a halo pattern was observed but sharp diffraction spots and rings were scarcely seen. This observation indicates that carbon was in an amorphous state. The photoelectron spectrum from the specimen with thin carbon film is shown in Fig. 1(a). Peaks of the C 1s and W 4f photoelectrons were observed, while no clear peaks were seen for impurities such as oxygen. Details of the W 4f spectrum are shown in (b) of this figure, in which the binding energy of W 4f$_{7/2}$ electrons is 31.2 eV, corresponding to that in metallic tungsten [7]. Therefore, it was concluded that the amorphous carbon film was directly deposited onto the tungsten surface without any intermediate layer such as the tungsten oxide film. It is probable that tungsten oxide was evaporated owing to the increase in the surface temperature and/or reduced to metallic tungsten by high temperature carbon atoms during deposition.



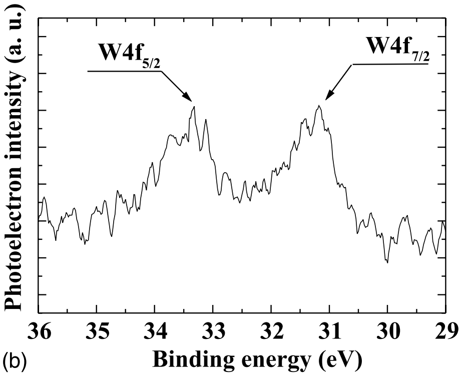


Fig. 1. (a) Photoelectron spectrum of a tungsten specimen with thin carbon film. (b) Details of the W 4f photoelectron spectrum.

Fig. 2(a) shows the XRD pattern before the heat treatment. All peaks observed were assigned to tungsten and aluminum used as the specimen holder. After heating at 973 K, no significant change was observed in the XRD patterns up to 240 min. At 1073 K, however, new peaks appeared after the heat treatment for 4 min or a longer period of time as shown in Fig. 2(b). These new peaks were assigned to W_2C. No peaks of WC were observed. The time dependence of W_2C growth was examined by measuring the peak intensity ratio of W_2C (0 4 0) planes to tungsten (2 2 0) planes (61.8° and 87.1°)

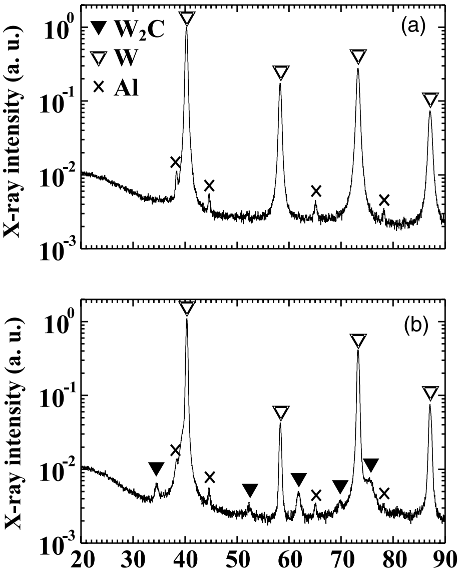


Fig. 2. XRD pattern from specimen surface before (a) and after heat treatment at 1073 K for 30 min (b).

because the intensity ratio between them was scarcely dependent on the incident direction of X-rays. Fig. 3 shows the change in the peak intensity ratio, $I(W_2C)/I(W)$, with time. After the induction period for ≈1 min, the amount of W_2C first increased with time, took the maximum value at 50 min and then decreased. This observation indicates that the reaction between the amorphous carbon film and the tungsten substrate progressed in the following three steps: nucleation, growth and decomposition of W_2C. The time dependence of W_2C growth at 1173 K is also shown in this figure. The amount of W_2C increased quickly, took the maximum value at 1 min and decreased rapidly. Peaks of WC were not observed at this temperature, either.

In secondary electron images observed by SAM, no significant contrast was observed on the surface of the specimen heated at 1073 K for 70 min. Hence, Auger electron spectra were acquired from the several randomly selected points with a primary electron beam of ≈10 nm in diameter. A typical example of the obtained Auger spectra is shown in Fig. 4. The carbon KLL spectrum have three peaks at 253, 258 and 268 eV. The heights of these peaks from background are comparable to each other. According to Childs et al. [8], the KLL spectrum from elemental carbon shows a single peak at around 253 eV with a shoulder in higher energy region, while that from tungsten carbide has three peaks. The intensity of the 268 eV peak, however, is significantly higher than that of other peaks in the C KLL spectrum from tungsten carbide shown by Childs et al. [8]. Hence, it is plausible that a small portion of carbon remained in an elemental state but the majority was present as tungsten carbide, W_2C. No significant difference was observed among all analyzed points in the shape of the C KLL spectrum and the peak-to-peak height ratio of carbon to tungsten. These observations indicate that the reaction between carbon and tungsten progressed uniformly in macroscopic scale under the present experimental conditions.

For comparison, a specimen sheet with C(H) film was prepared in the manner described in the previous paper [4] and heated at 1073 K for 10 and 30 min. The peaks of W_2C appeared after heating, while no peaks of WC were observed. Hence, hydrogen in carbon film does not appear to alter the reaction product at this temperature, although detailed examinations of time dependence of reaction are necessary to derive a final conclusion.

It should be emphasized that W_2C was formed from both of carbon films with and without hydrogen deposited under quite different conditions. This is because W_2C is thermodynamically stable above 1523 K in the case of the graphite–tungsten system, and WC is the only stable carbide at the present temperature range [9]. Hence, it is concluded that the rates of nucleation and growth of W_2C are significantly higher than those of WC at these temperatures. Luthin and Linsmeier [5,6] also reported that W_2C growth took place at 770 K

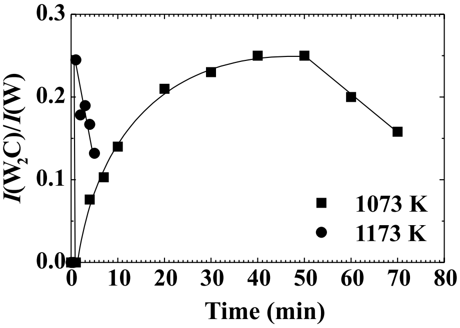


Fig. 3. Change in the peak intensity ratio of W_2C to tungsten with elapse of time. Solid lines are guides to the eyes.

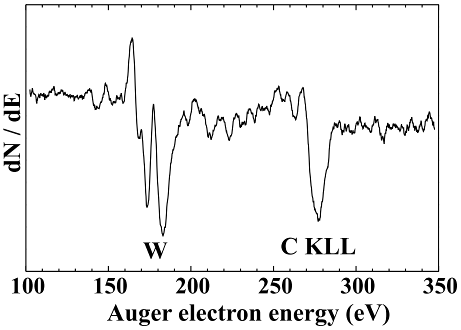


Fig. 4. Typical example of an Auger electron spectrum after heat treatment at 1073 K for 70 min.

and higher temperatures through the reaction between tungsten and the thin carbon film, although the deposition rate in their study was much smaller than the present one; the deposition rate in their study was 0.01–0.04 nm min^{-1} [5,6]. Therefore, W_2C appears to be formed from deposited films at the present temperature range under wide variety of deposition conditions. The mechanisms underlying metastable W_2C nucleation and growth, however, are not understood at present. Therefore, systematic studies with well-characterized carbon films are required.

In the previous study [4], the reaction between the C(H) film and residual water vapor was observed above 600 K. It is therefore probable that the decomposition of W_2C shown in Fig. 3 was caused by the reaction between carbon in W_2C and the water vapor in the vacuum system. Luthin and Linsmeier [5,6] reported that significant diffusion of carbon into tungsten takes place above 970 K. In the present case, however, the dissolution of carbon in the tungsten phase appears to make only negligibly small contribution to W_2C decomposition. This is because the solubility of carbon in tungsten is significantly small in comparison with the amount of deposited carbon at the temperature range examined in the present study. The solubility of carbon in tungsten in equilibrium with W_2C has been measured by Goldschmidt and Brand [10] and Gebhardt et al. [11], and the latter group has reported higher values. According to Gebhardt et al. [11], the solubility of carbon in tungsten is 0.101–0.625 mol.% at temperatures between 2068 and 2913 K. The solubility at 1073 K is estimated to be 1 mol ppm by extrapolating their data. Hence, the possible amount of carbon dissolved in the specimen is evaluated to be 3×10^{-9} mol. On the other hand, the amount of carbon deposited was $\approx 1 \times 10^{-7}$ mol. Namely, only 3% of carbon can be dissolved in the tungsten phase. In Fig. 3, however, $I(W_2C)/I(W)$ decreased from 0.25 (50 min) to 0.16 (70 min); the amount of W_2C decreased by 36% within 20 min. In order to confirm the occurrence of the reaction between carbon and water vapor in the residual gas, 10 g of W_2C powder was heated at 1073 K for 10 h in the same vacuum system and analyzed by means of XRD. This powder contained WC and metallic tungsten as impurities, and the concentrations of W_2C, WC and W were 59, 3 and 38 mol.% before heat treatment. After heating, the concentrations of W_2C, WC and metallic tungsten became 30, 4 and 66 mol.%, respectively. Namely, the concentration of W_2C decreased significantly, while that of metallic tungsten increased. This observation indicated that carbon was removed from W_2C phase by the reaction with residual gas. The mass of powder decreased by 0.0135 g by removal of carbon. The estimation of the powder surface area from the particle size and the mass analysis of residual gas showed that only the partial pressure of water vapor was high enough to remove 0.0135 g of carbon within 10 h. Therefore, it is apparent that carbon was removed through the reaction with water vapor.

The transformation from metastable W_2C to stable WC was not observed in the present study, because the reaction between carbon and water vapor in the residual gas took place prior to this transformation as mentioned above. In contrast to our results, Luthin and Linsmeier [5,6] observed not only W_2C but also WC by XPS as described in Section 1. According to them [5,6], WC was formed during carbon film deposition at room temperature and grew during heat treatments. Namely, the fraction of carbon present as WC was initially 5%, and it started to increase at 870 K and reached to ≈80% at 1270 K [5]. It is, however, still an open question whether the significant growth of WC takes place under the conditions examined by Luthin and Linsmeier [5,6]. In their study, the increase in the WC fraction was accompanied by a significant decrease in the total amount of carbon at the surface caused by the diffusion into tungsten. Under such condition, the decrease in the amount of elemental carbon and W_2C can lead to the increase in the fraction of WC. Namely, the fraction of WC can increase without any growth of WC. The rate of transformation from W_2C to WC should be examined under the conditions where no significant amount of carbon is removed from the reaction layer by either of reaction with residual gas and dissolution into tungsten phase.

4. Conclusions

The solid state reaction between tungsten and amorphous carbon was studied at 973, 1073 and 1173 K by XRD. No carbide appeared at 973 K within 240 min. On the other hand, the peaks of W_2C appeared at 1073 and 1173 K after an induction period, although W_2C is thermodynamically not stable at these temperatures. The intensities of W_2C peaks increased with elapse of time and then decreased owing to the decomposition of W_2C. No diffraction peak from WC was detected at both temperatures. These results indicated that the rates of nucleation and growth of W_2C are significantly higher than those of WC at these temperatures.

References

[1] R. Behrisch, A.P. Martinelli, S. Grigull, R. Grötzschel, U. Kreissig, D. Hildebrandt, W. Schneider, J. Nucl. Mater. 220–222 (1995) 590.

[2] A. Sagara et al., J. Nucl. Mater. 241–243 (1997) 972.

[3] N. Noda, V. Philips, R. Nue, J. Nucl. Mater. 241–243 (1997) 227.

[4] K. Ashida, K. Fujino, T. Okabe, M. Matsuyama, K. Watanabe, J. Nucl. Mater. 290–293 (2001) 42.

[5] J. Luthin, Ch. Linsmeier, Surf. Sci. 454–456 (2000) 78.

[6] J. Luthin, C.h. Linsmeier, J. Nucl. Mater. 290–293 (2001) 121.

[7] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Prairie, MN, 1979.

[8] K.D. Childs, B.A. Carlson, L.A. La Vanier, J.F. Moulder, D.F. Paul, W.F. Stickle, D.G. Watson, in: C.L. Hedberg (Ed.), Handbook of Auger Electron Spectroscopy, Physical Electronics, Eden Prairie, MN, 1995.

[9] T.B. Massalski, Binary Alloy Phase Diagrams, 2nd Ed., American Society of Metals, Metals Park, OH, 1990.

[10] H.J. Goldschmidt, J.A. Brand, J. Less-Common Met. 5 (1963) 181.

[11] E. Gebhardt, E. Fromm, U. Roy, Z. Metallkd. 57 (1966) 732.