

論文

タングステンとアモルファス炭素膜との固相反応

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Solid State Reaction between Tungsten and Amorphous Carbon Film

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Abstract

Solid state reaction between tungsten and carbon film was examined at 1073 K. Carbon film was deposited onto tungsten sheet by vacuum evaporation at room temperature and analyzed by means of X-ray photoelectron spectroscopy. Carbon and tungsten beneath the carbon film were detected, whereas only trace amount of impurities such as oxygen were present. The binding energy of W 4f electrons indicated that tungsten was in a metallic state at the interface. These observations suggested that no impurity layer existed at the interface. Analysis using transmission electron microscopy showed that carbon was in an amorphous state. The specimen was heated at 1073 K in vacuum, and change in crystal structure was analyzed by means of X-ray diffraction. The peaks of W_2C appeared after an induction period for ca. 1 min, although W_2C is not thermodynamically stable at 1073 K. The peak intensity ratio of W_2C to metallic

tungsten increased in proportion to the square root of time to take the maximum value at 50 min and then decreased with elapse of time. No peak of WC was observed. These results indicate that the nucleation rate of W_2C was much faster than that of WC at 1073 K. The decomposition of W_2C was ascribed to the reaction between carbon in W_2C and H_2O in residual gas.

1. Introduction

Low-Z materials such as carbon and beryllium are widely used for plasma-facing components in magnetic confinement fusion devices to reduce radiation loss from plasma [1, 2]. These materials, however, have high erosion rates through chemical and physical sputtering and evaporation. 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 in many fusion devices to use two or more plasma facing materials being complementary to each other. Sputtering and evaporation of one plasma facing material should result in deposition onto the surfaces of other materials and modification of their surface properties. Fuel recycling and inventory become complicated through such surface modification of plasma facing components. An understanding of properties of such deposited layer is necessary for the selection of plasma facing materials in next generation fusion devices.

In the previous paper [4], carbon films containing hydrogen were deposited onto tungsten sheets as a model system to simulate the properties of co-deposited layer on the surface of tungsten divertor, and solid state reactions between the carbon film and the tungsten substrate were examined at temperatures from 300 to 1273 K by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). Carbon started to react with tungsten at ca. 900 K to form tungsten carbide, W_2C , and a large amount of hydrogen was released through this reaction. These observations suggest that fuel recycling and inventory at tungsten divertors are strongly affected by the reaction between tungsten and carbon. The reaction kinetics, however, has not been studied in detail. The influence of hydrogen on the reaction has not been clarified. Therefore, the study of the reaction kinetics is necessary for tungsten and carbon film with and without hydrogen.

In the present study, carbon film without hydrogen was deposited on tungsten by vacuum evaporation and characterized by means of XPS and transmission electron microscopy. Then the specimen was heated in vacuum at 1073 K and the reaction kinetics was examined by use of X-ray diffraction (XRD).

2. Experimental

2.1. Specimen preparation and characterization

Tungsten specimens measuring $10 \times 10 \times 0.3$ mm were cut from sheets supplied by Nilaco (99.95 mass% in purity). The surfaces of the specimens were polished with SiC papers and finished with $0.3 \mu\text{m}$ Al_2O_3 powder. The carbon film of ca. 10 nm thickness was deposited onto the specimen surface with a conventional carbon evaporator evacuated with an

oil-sealed rotary pump, in which the tip of a sharpened carbon rod was pressed against a flat cross section of another carbon rod by a spring. Carbon was evaporated by ohmic heating of the tip at 4.5 V for 2 min. The specimen was rotated during deposition. The thickness of the film was estimated from the mass loss of the sharpened carbon rod and the geometrical arrangement between the tip and the specimen by assuming that the film was deposited uniformly. The density of deposited film was presumed to be 2.0 g/cm^3 in this estimation. This is because the deposited carbon was in amorphous state as described in 3.1, and the density of amorphous carbon is $1.8\text{-}2.1 \text{ g/cm}^3$ [5].

The crystal structure of carbon film was examined with a transmission electron microscope (TEM) of Faculty of Engineering, Toyama University. Here, a carbon film was deposited onto a tungsten mesh made of wires of $20 \mu\text{m}$ diameter, and the films deposited onto the edge of wires were observed. Acceleration voltage was adjusted to 200 keV.

The carbon film and tungsten beneath the film were analyzed also by means of XPS. In this case, the specimen with a thin film (ca. 3 nm) was prepared by reduction of deposition time to 30 s in order to detect photoelectrons from tungsten and installed in an ultra high vacuum chamber. The analysis was carried out at room temperature without any surface treatment such as sputtering. Non-monochromatic Mg K_{α} X-rays (1253.6 eV) were used for photoelectron excitation. The power of X-ray source was adjusted to 400 W. The energy spectrum of photoelectrons was measured with a double pass cylindrical mirror analyzer.

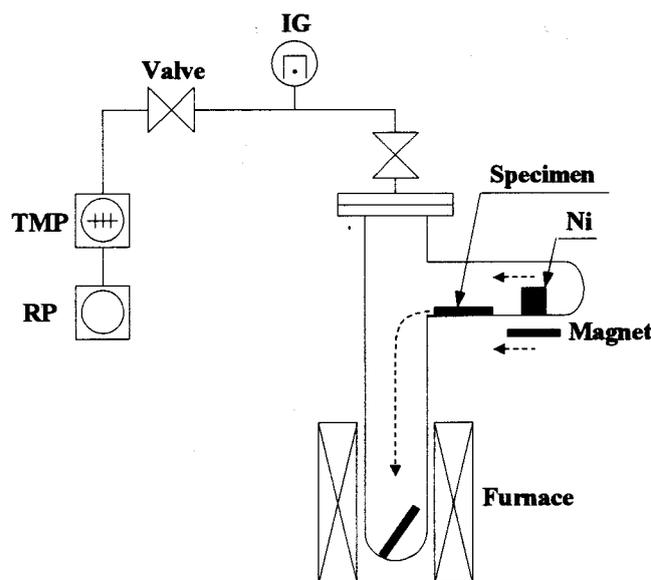


Fig. 1 Schematics of apparatus for heat treatment.

2.2. Heat treatment and XRD analysis

The specimen with a carbon film of ca. 10 nm thickness was heated at 1073 K for 1 to 70 min in vacuum with the apparatus shown in Fig. 1. This apparatus consists of a quartz tube with a branch tube, a turbo molecular pump (TMP), an oil-sealed rotary pump (RP), an ionization gauge (IG) and a furnace. The specimen was first installed in the branch tube with a nickel piece. After evacuation, the quartz tube was heated with the furnace to 1073 K. Then the specimen was pushed by moving the nickel piece with a magnet and dropped into the main tube when residual pressure reached to 1.1×10^{-5} Pa or lower. The change in specimen color after the drop showed that the specimen temperature reached to 1073 K within 20 s. The specimen was heated for a designed period of time and cooled by removing the furnace.

After the 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 K_α X-rays. The incident angle of X-rays was adjusted to 1.5° to analyze a shallow region from the surface. It was estimated from the density and the mass absorption coefficient of tungsten [6] that the intensity of diffraction peak is attenuated to 1/10 at depth of ca. 100 nm and to 1/100 at ca. 200 nm in this geometrical arrangement.

3. Results and discussion

3.1. Chemical state of carbon and tungsten before heat treatment

Figure 2 shows the photoelectron spectrum from the specimen surface with carbon film of ca. 3 nm thickness. The peaks of C 1s and W 4f electrons are clearly observed. It should be emphasized that no clear peak was observed for oxygen and other impurities.

The spectrum of W 4f photoelectrons is shown Fig. 3. The binding energy of W $4f_{7/2}$ electrons was 31.2 eV. This energy corresponds to that of metallic tungsten [7]. The peaks of WO_2 (32.5 eV) and WO_3 (35.0-36.5 eV) [7] were not observed. Namely, no oxide layer was formed at the interface between the carbon film and the tungsten substrate although the carbon film

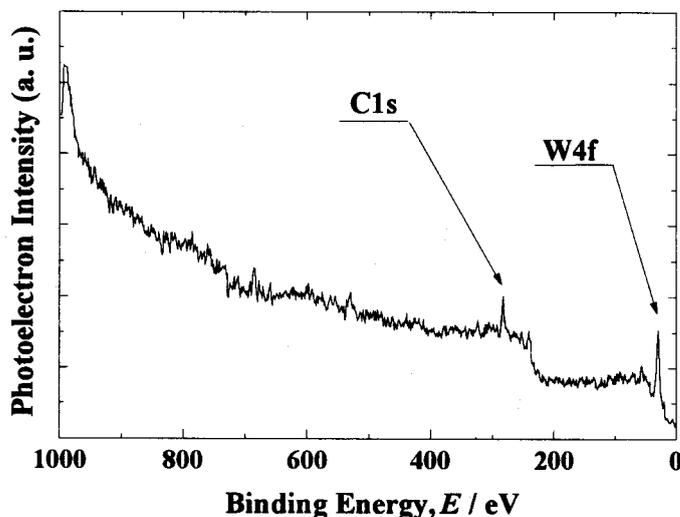


Fig. 2 Photoelectron spectrum from specimen with thin carbon film (ca. 3 nm).

was deposited without any surface treatments of substrate. It is appropriate to consider that tungsten oxide was evaporated owing to increase in surface temperature and/or reduced to metallic tungsten by high temperature carbon atoms impinging onto the tungsten surface.

The C 1s photoelectron spectrum is shown in Fig. 4. The binding energy of C 1s electrons was 284.8 eV. This binding energy corresponds to the state of disordered carbon reported by Reinke et al. [8]. In the TEM analysis, halo patterns were observed but sharp diffraction spots/rings were scarcely seen. Hence, it is concluded that carbon was in an amorphous state. Luthin and Linsmeier [9] have examined carbon films deposited on tungsten at room temperature by use of XPS. They reported that carbon existed as graphitic and disordered states, and the amount of carbon in the former state was larger than that in the latter. Such difference in the extent of crystallization during deposition is ascribed to the difference in the deposition rate. In the present study, the deposition rate was about 5 nm/min. On the other hand, it was 0.01-0.04 nm/min in their study [9]. Such high deposition rate employed in the present study should be the cause of disordering of carbon.

3.2. Reaction between tungsten and carbon Film

Figure 5 (a) shows the XRD pattern of the as-prepared specimen. All the peaks observed were assigned to tungsten and aluminum (specimen holder). High background signals at low diffraction angle region is due to direct incidence of X-rays to the detector. No significant change was observed in XRD pattern after the heat treatment at 1073 K for 1 min. New peaks, however, appeared after the heat treatment

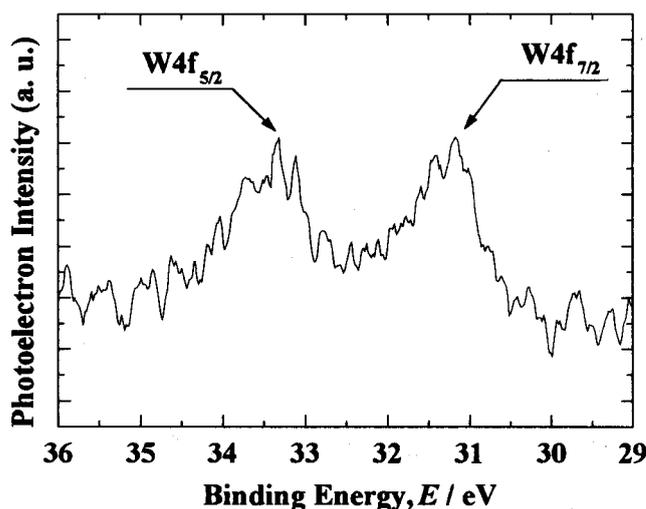


Fig. 3 Spectrum of W 4f photoelectrons.

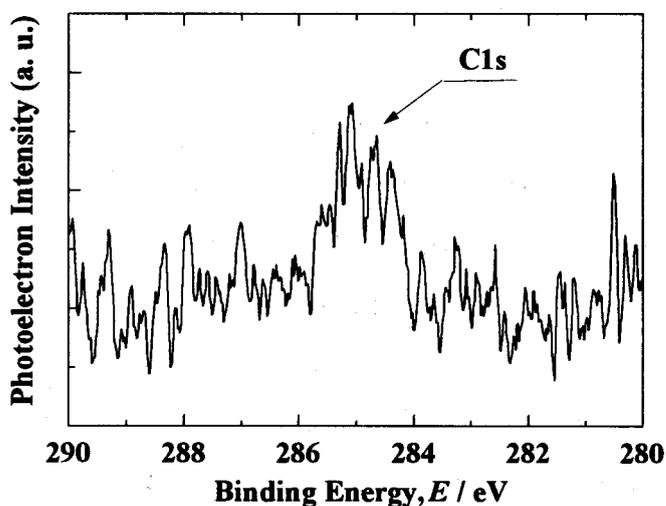


Fig. 4 Spectrum of C 1s photoelectrons.

for 4 min or longer period of time as shown in Figs. 5 (b) and (c). These new peaks were assigned to W_2C . No peak from WC was observed. The intensity ratios among tungsten peaks were dependent on the direction of the specimen against the pass of X-rays as shown in (b) and (c) of this figure as well as those among W_2C peaks because of preferred orientation of crystallites in the tungsten substrate. Hence, the peak intensity ratios between tungsten and W_2C also showed such dependence on X-rays incident direction. The intensity ratio between tungsten (220) and W_2C (040) peaks showed the smallest dependence on the incident direction of X-rays. Therefore, the change in the amount of W_2C with heat treatment time was examined by measuring the intensity ratio between these two peaks, $I_{W_2C(040)} / I_{W(220)}$. The specimen was always set on the holder in the same direction in the reaction kinetics examination. The change in $I_{W_2C(040)} / I_{W(220)}$ with time is shown in

Fig. 6. After the induction period of 1 min, the amount of W_2C first increased with time, took the maximum value at 50 min and then decreased. The period of time necessary to increase the specimen temperature up to 1073 K was less than 20 s as mentioned above. So, the observation of the induction period of ca. 1 min indicates that nucleation and growth of W_2C up to detectable size of XRD takes several tens seconds at

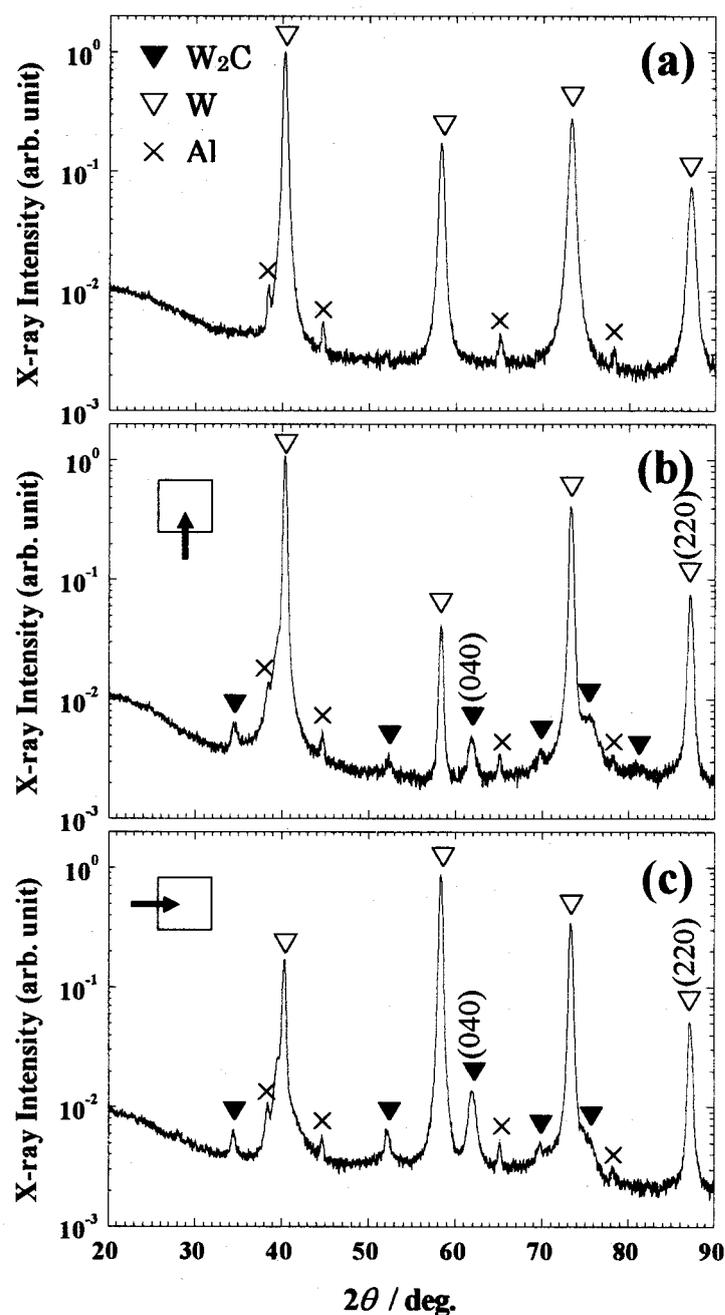


Fig. 5 Results of XRD analyses; (a): before heat treatment, (b): after heat treatment for 30 min, and (c): as (b) but with different incident direction of X-rays.

1073 K. The reduction in $I_{W_2C(040)}/I_{W(220)}$ observed in the region above 50 min suggests the growth of W_2C was followed by decomposition of this phase.

According to the phase diagram of W-C system [10], W_2C is thermodynamically stable only above 1523 K, whereas WC is stable at 1073 K. Hence, the observation of metastable W_2C indicates that the nucleation rate of W_2C was much faster than that of WC in the reaction between carbon film and tungsten substrate. In the previous study on the reaction between the hydrogen-containing carbon film and the tungsten substrate at 300-1273 K [4],

W_2C was formed at temperatures above 900 K but WC was not observed as described in section 1.

Namely, no significant difference was observed in the reaction product between the carbon films with and without hydrogen. Luthin and Linsmeier [9] also examined the reaction between the carbon film and tungsten by annealing the specimen at temperatures from 300 to 1270 K for 30 min. They reported that carbon mainly existed as W_2C at the

temperature range from 900 to 1170 K and as WC at higher temperatures [9]. The present observation of W_2C at 1073 K is in good agreement with their results although the initial crystal structure of carbon is different as mentioned in the previous section.

Hence, it can be concluded that the nucleation rate of W_2C is faster at 1073 K than that of WC in the reaction of tungsten with a wide

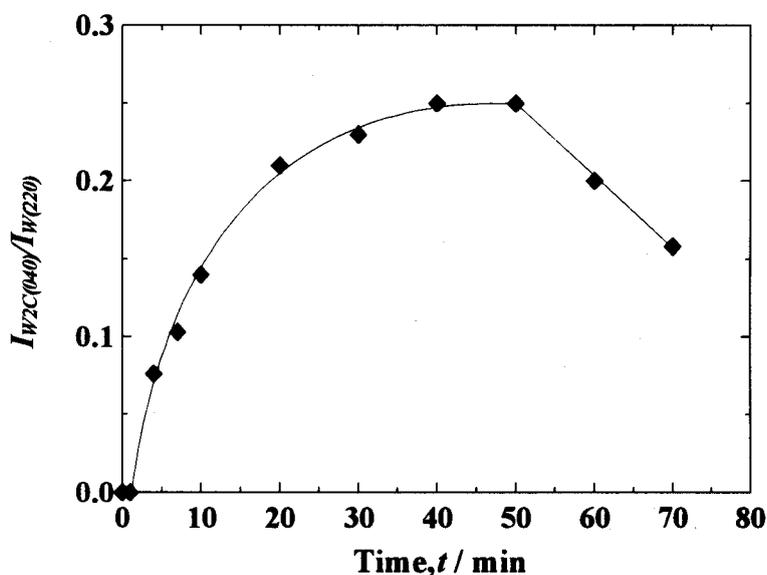


Fig. 6 Change in amount of W_2C with time.

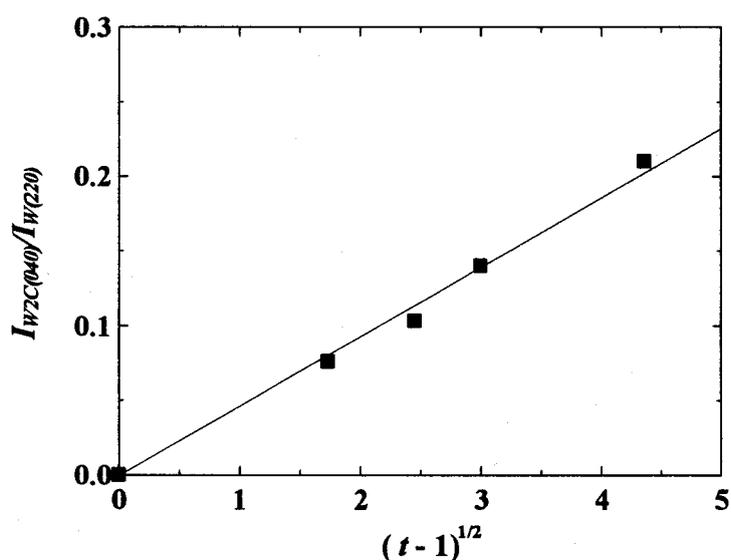


Fig. 7 Plot of $I_{W_2C(040)}/I_{W(220)}$ against the square root on time after induction period.

variety of carbon films. At higher temperatures, however, an initial hydrogen content and/or crystal structure of carbon film seem to have influence on reaction product because no WC was observed in the previous study [4] even at 1273 K. Further investigation is required for the temperature dependence of reaction product. The reaction kinetics was not examined in detail in the previous study [4] and the study of Luthin and Linsmeier [9]. Hence, it is difficult at the present to discuss the influence of hydrogen content and initial crystal structure on the reaction kinetics. Takatsu [11] who has examined the reaction between tungsten and CH_4 in the temperature range from 1073 to 1473 K reported that WC was the main reaction product and only a small amount of W_2C was observed at the metal-carbide interface. This observation indicates that the relation between nucleation rates of W_2C and WC at 1073 K is different between solid state reactions and gas-solid reactions.

In the early stage of the reaction, $I_{\text{W}_2\text{C}(040)} / I_{\text{W}(220)}$ increased in proportion to the square root of heat treatment time as shown in Fig. 7. Namely, the time course of W_2C growth was described as

$$I_{\text{W}_2\text{C}(040)} / I_{\text{W}(220)} = k(t-t_i)^{1/2}, \quad (1)$$

where k is the rate constant, t the heat treatment time, t_i the length of induction period being ca. 1 min at 1073 K. Such parabolic time dependence is usually observed when the growth of uniform film is controlled by diffusion process of a reactant. The rate constant k at this temperature was determined to be $0.046 / \text{min}^{1/2}$ from the gradient of the line in this figure. The measurements of k at different temperatures are in progress at the present. The rate controlling process can be deduced by comparing the activation energy of reaction with that of grain and grain boundary diffusion of tungsten and carbon in W_2C . The examination of uniformity of W_2C growth is

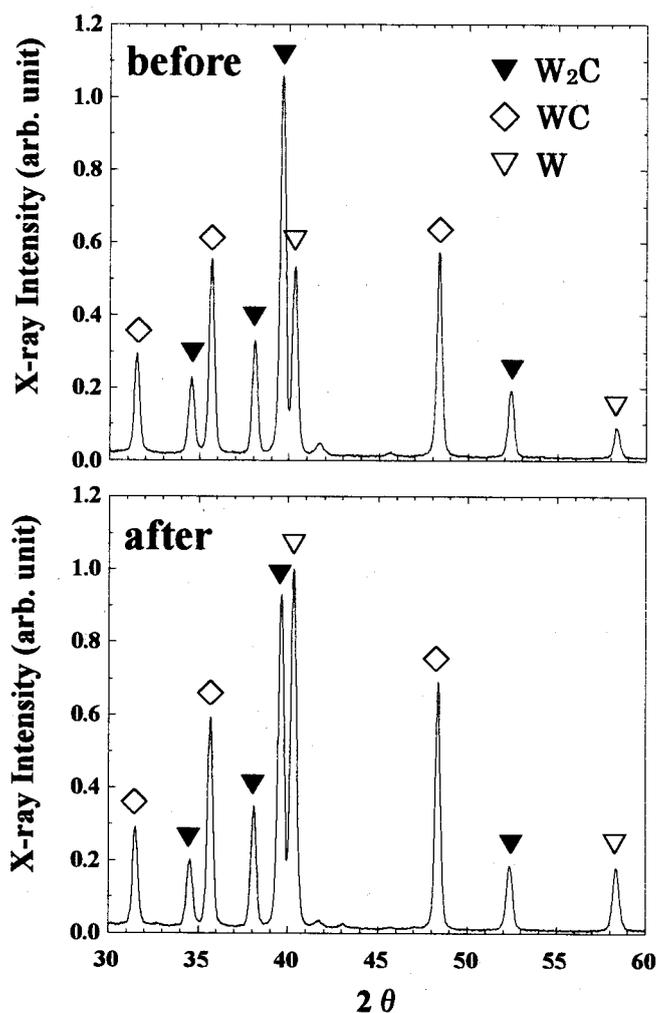


Fig. 8 XRD pattern of W_2C powder before and after heat treatment at 1073 K for 10 h in vacuum.

also necessary.

The decomposition of W_2C cannot be ascribed to the dissolution of carbon into tungsten phase, because the solubility of carbon in tungsten is low at 1073 K. The solubility of carbon in tungsten in equilibrium with W_2C has been measured by Goldschmidt and Brand [12] and Gebhardt et al. [13], and the latter group has reported higher values. According to Gebhardt et al. [13], 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 ca. 1×10^{-7} mol. Namely, only 3 % of carbon can be dissolved in the tungsten phase. In Fig.6, however, $I_{W_2C(040)} / I_{w(220)}$ decreased from 0.25 (50 min) to 0.16 (70 min); the amount of W_2C decreased by 36 % within 20 min. Therefore, the decomposition of W_2C is attributed to the oxidation of carbon by residual gases such as H_2O and O_2 . In order to remove 36 % of carbon from the specimen surface within 20 min, the flux of reactant must be higher than 3×10^{-7} mol/m²·s. Hence, the partial pressure of reactant should be in order of or higher than 10^{-5} Pa; the partial pressure of reactant must be comparable to the total pressure. Mass analysis of residual gas showed that H_2O was the dominant component of the residual gas, and the partial pressures of other gases were lower than that of H_2O by one order of magnitude or more. Therefore, the decomposition of W_2C is ascribed to the reaction between carbon and H_2O .

In order to confirm the occurrence of the reaction between carbon and H_2O in residual gas, 10 g of W_2C powder purchased from Kojundo Chemical Lab was heated at 1073 K for 10 h in the apparatus shown in Fig. 1. This powder contained WC and metallic tungsten as impurities. The change in concentration ratio among W_2C , WC and metallic tungsten by heating was measured by means of XRD. The results are shown in Fig. 8. Before heating, the peak from (102) plane of W_2C (39.6°) was highest in intensity. The relation between concentrations and peak intensity ratios among W_2C , WC and metallic tungsten was examined by measuring XRD patterns of several mixture powders prepared by addition of known amounts of WC and W to W_2C . The concentrations of W_2C , WC and metallic tungsten in the specimen powder thus determined were 59, 3 and 38 mol%, respectively. After heating, however, the intensity of W_2C (102) peak was lower than that of the peak from W (110) plane (40.3°). The concentrations of W_2C , WC and metallic tungsten were 30, 4 and 66 mol%, respectively. Namely, the concentration of W_2C decreased significantly, while that of metallic tungsten increased. Therefore, it is apparent that carbon was removed from W_2C phase by the reaction with residual gas. The mass of powder decreased by 0.0135 g by heating. The estimation of surface area of powder from particle size showed that

the partial pressure of reactant has to be in order of or higher than 10^{-5} Pa also in this case to remove 0.0135 g of carbon within 10 h. Therefore, the dominant reactant is considered to be H_2O also in this case. It is necessary to measure the decomposition rate of W_2C under controlled H_2O partial pressure.

4. Conclusions

The solid state reaction between tungsten and carbon film was examined at 1073 K. The carbon film was deposited onto the tungsten sheet in vacuum at room temperature, and the deposited film and tungsten at the interface were analyzed by means of XPS and TEM. The binding energy of W 4f electrons indicated that tungsten was in a metallic state. This observation suggested that no impurity layer existed at the interface. The binding energy of C 1s electrons and the result of TEM observation suggested that carbon was in an amorphous state. The peaks of W_2C appeared after induction period of ca. 1 min by heating the specimen at 1073 K in vacuum, although W_2C is thermodynamically unstable at this temperature. The peak intensity ratio of W_2C to tungsten increased in proportion to the square root of time to take the maximum value at 50 min and decreased in proportion to time. No peak of WC which is thermodynamically stable at 1073 K was detected. These observations indicate that the nucleation rate of W_2C was much faster than that of WC. The decomposition of W_2C was ascribed to the reaction between carbon in W_2C phase and H_2O in residual gas.

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