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Influence of microstructure of tungsten on solid state reaction rate with amorphous carbon film

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Abstract

Plate-type specimens were cut from three different types of tungsten sheets fabricated under distinct rolling and heat treatment conditions in the directions parallel or perpendicular to the rolling planes. Amorphous carbon films were prepared by vacuum deposition on the specimen surfaces. Then, the specimens were heated at 1073 K in vacuum, and reaction products were analyzed by means of X-ray diffraction. The carbide formed was W_2C and no peak of WC appeared. The growth rate of W_2C was independent of the cutting directions of the specimens, although the grain boundary densities at the specimen surfaces were quite different. On the other hand, the rate of W_2C growth was dependent on both reduction and heat treatment conditions, and a specimen with higher hardness showed a higher growth rate. By taking account of the observations by a transmission electron microscope, it was concluded that dislocations play important roles in W_2C growth.

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Keywords: Tungsten; Carbide; Carbon impurities; Co-deposition; Materials properties

1. Introduction

Installation of two or more plasma facing materials is common now in many fusion devices to control plasma-surface interactions. For example, beryllium, carbon and tungsten would be used for in-vessel components of ITER [1]. Under such conditions, erosion of one plasma-facing material results in the deposition onto the surfaces of coexisting materials to modify their physical and chemical properties. Hence, it is important to understand the properties of modified materials and the mechanism underlying the modification.

The modification of tungsten by carbon deposition has been examined by several researchers [2–7]. In most cases of these studies, the formation of tungsten carbide was observed at elevated temperatures [2–6]. The growth of tungsten carbide should cause the change in fuel recycling and lead to degradation in many important properties of tungsten such as melting point and thermal conductivity [8]. Hence, it is strongly required to clarify the mechanisms of the reactions between tungsten and

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Table 1
List of specimens

Sheet type	Specimen type	Reduction (%)	Thickness (mm)	Heat treatment	Plane examined	Hv
A	T5-RP	82	5	SR	RP	437
	T5-NP	82	5	SR	NP	443
B	T1-SR	95	1	SR	RP	484
C	T1-RX	95	1	RX	RP	381

Hv: Vickers hardness.

carbon. It is known that polycrystalline tungsten is carburized more easily than single crystal [9]. This fact suggests that grain boundaries and other defects enhance carburization. Yeh et al. [10] have examined the reaction of tungsten thin films with diamond substrate at 1073–1373 K with various analysis techniques and concluded that grain boundary diffusion of carbon in tungsten played an important role in the reaction. On the other hand, according to Tao [11] who has investigated the reaction of coarse tungsten powder with carbon at 1573–2173 K, the carburization proceeded uniformly from the surfaces of powder particles in most cases, and that along grain boundaries was rarely observed. Such significant discrepancy can be ascribed to the difference in microstructures of specimens and reaction conditions such as temperature. Therefore, systematic studies under a wide variety of reaction conditions with well-characterized specimens are necessary to understand the reaction mechanism.

In the present study, the attention was focused on the influence of microstructure of tungsten on the reaction with carbon. Four types of tungsten specimens having different microstructures were prepared by changing fabrication conditions, and the reaction with an amorphous carbon film was examined at 1073 K. The influence of grain boundaries and dislocations on the carbide growth rate was discussed.

2. Experimental

Three different types of tungsten sheets were supplied by A. L. M. T. Co.; they were prepared by sintering followed by warm-rolling to 82% or 95% and heat treatments. The thicknesses of the sheets were 5 mm (82% reduction) and 1 mm (95% reduction). The sheets of former thickness are hereafter denoted as T5 and those of the latter as T1. The first type of sheets (A) was prepared by stress-relief (SR) annealing of T5 at 1473 K for 3.6 ks. The second type (B) was obtained by SR annealing of T1 at 1173 K for 1.8 ks, and the third type (C) by recrystallization (RX) annealing of T1 at 1573 K for 3.6 ks. The purity of the sheets was 99.99 mass%. Main impurities were Mo (12 ppm), carbon (10 ppm), nitrogen (10 ppm), oxygen (<10 ppm), Fe (6 ppm) and Si (<5 ppm).

Four kinds of plate-type specimens were prepared from the above-mentioned three types of sheets as summarized in Table 1. In the case of T5 sheets, the specimens were cut in directions parallel or normal to the rolling planes to examine the influence of grain boundary density on the reaction rate with carbon film. As described later, the crystal grains were severely compressed in the normal direction against the rolling plane, and hence the grain boundary density was higher in the latter specimen than the former. The size of the former specimens was $10 \times 10 \times 1$ mm^3 and that of the latter $5 \times 20 \times 1$ mm^3. These specimens are hereafter described as T5-RP (rolling plane) and T5-NP (normal plane). In the cases of T1 sheets prepared by SR or RX annealing, the specimens of $10 \times 10 \times 1$ mm^3 were cut in parallel with rolling plane. These specimens are denoted as T1-SR and T1-RX.

The surfaces of specimens were polished with abrasive papers and finished with fine Al_2O_3 powder from 3 to 0.06 μmin diameter. Amorphous carbon films of 10 nm thickness were prepared on the specimen surfaces at room temperature with a conventional carbon evaporator evacuated by an oil-sealed rotary pump. In order to examine the chemical state of tungsten at tungsten/carbon interface, the specimen with thinner carbon film (3 nm) was prepared and analyzed with X-ray photoelectron spectroscopy [6]. The peak of W $4f_{7/2}$ photoelectrons appeared at 31.2 eV, indicating major part of tungsten was in a metallic state. The specimens thus prepared were heated at 1073 K in vacuum, where the pressure of residual gas was below 1×10^{-5} Pa. Reaction products were analyzed by means of grazing angle X-ray diffraction (XRD) with Cu Kα radiation. Incident angle of X-rays was adjusted to be 1.5°.

In order to examine the microstructures, the surfaces of some specimens were etched by an aqueous solution of KOH and $K_3[Fe(CN)_6]$ (0.1 g/cm^3 for each) and observed with an optical microscope. Vickers hardness was measured at a load of 500 g.

3. Results and discussion

Micrographs of specimens are shown in Fig. 1. Comparison between T5-RP and T5-NP clearly shows that the grain boundary density was higher for the latter than

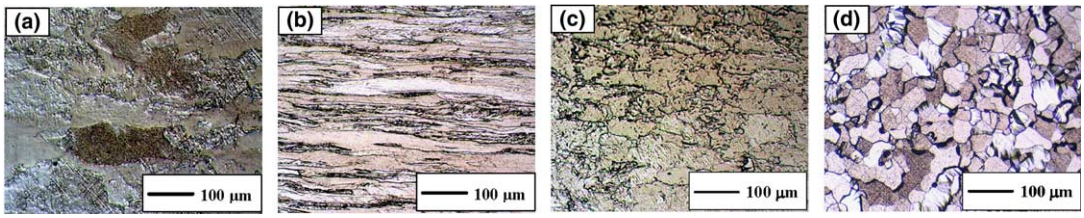

Fig. 1. Micrographs of specimens: (a) T5-RP, (b) T5-NP, (c) T1-SR and (d) T1-RX.

the former. This is because the crystal grains were severely compressed during rolling. The crystal grains of T1-SR were elongated, while equiaxed grains were developed in T1-RX by recrystallization annealing. Vickers hardness of T1-SR was higher than that of T5 specimens because of higher reduction as summarized in Table 1, whereas T1-RX showed significantly smaller hardness than T1-SR owing to recrystallization.

Fig. 2 shows the XRD pattern of T5-RP after reaction with the amorphous carbon film at 1073 K for 160 min as a typical example. The peaks observed were assigned to W_2C [12], W [13] and Al [14] used as sample holder, and no peak of WC was observed. This result is consistent with the observations in the previous studies [4,6]. The time dependence of W_2C growth was examined by comparing the peak intensities between the W_2C (300) and tungsten (220) planes because these two peaks had enough high intensity and did not overlap with other peaks. This peak intensity ratio, $I(W_2C)/I(W)$, was dependent on the incidence direction of X-rays because the specimens had crystal textures. Hence, for every specimen, the XRD patterns were examined two times with the incident directions parallel with and normal against rolling direction.

The change in $I(W_2C)/I(W)$ of T5-RP and T5-NP are plotted in Fig. 3 against reaction time. Although the

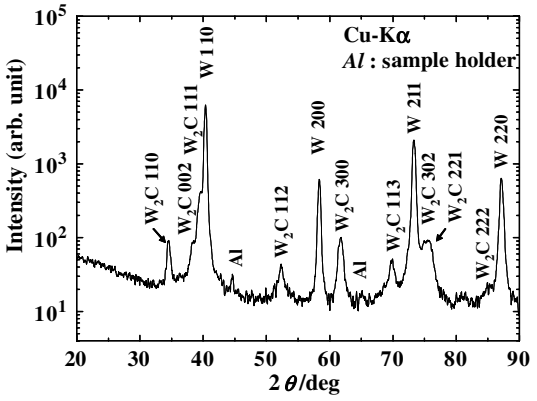

Fig. 2. Typical example of XRD pattern after reaction with amorphous carbon film at 1073 K (specimen: T5-RP, reaction time: 160 min).

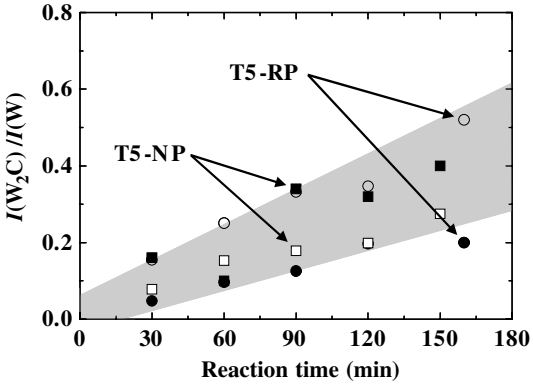

Fig. 3. Change in $I(W_2C)/I(W)$ of T5-RP and T5-NP with reaction time. Open and filled symbols correspond to parallel and normal X-ray incidence with/against rolling direction, respectively. Gray zone is a guide to eyes.

grain boundary density at the surfaces of the former specimen was significantly smaller than that of the latter, no significant difference was observed in the development of $I(W_2C)/I(W)$ ratio within the dispersion of the data. This observation indicates that the influence of grain boundaries on W_2C growth is minor under the present conditions.

Fig. 4 shows the change in $I(W_2C)/I(W)$ ofT1-SR and T1-RX. In this case, the development of $I(W_2C)/I(W)$ ratio was significantly slower for T1-RX than T1-SR. Namely, the growth rate of W_2C was reduced by recrystallization. It should be noted here that such tendency was indicated not only by comparison between W_2C (300) and W (220) peaks shown in this figure but also by other pairs of W_2C and W peaks. A comparison between Figs. 3 and 4 showed a correlation between $I(W_2C)/I(W)$ and hardness. Namely, when the specimens are arranged in the descending order of hardness as T1-SR, T5 specimens (T5-RP and T5-NP) and T1-RX, the same order holds for the reduction in the $I(W_2C)/I(W)$ development, leading to a conclusion that the specimen with higher hardness has higher reactivity with carbon.

To clarify the mechanism underlying the influence of recrystallization on the rate of reaction with carbon, the microstructures of T1-SR and T1-RX were examined

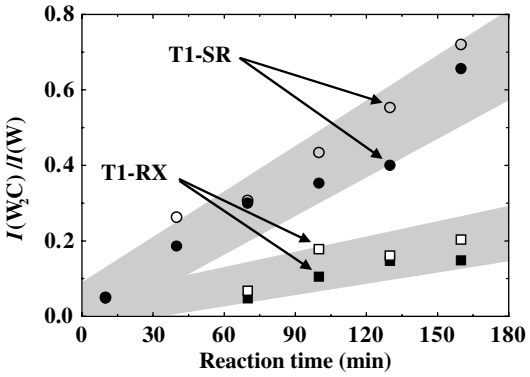

Fig. 4. Change in $I(W_2C)/I(W)$ of T1-SR and T1-RX with reaction time. Open and filled symbols correspond to parallel and normal X-ray incidence with/against rolling direction, respectively. Gray zones are guides to eyes.

also by a transmission electron microscope (TEM), where the specimens were prepared by milling with 8 keV Ar ions at incident angle of 8°. As shown in Fig. 5, dislocations tangled with each other were observed in T1-SR in high density, while no clear dislocations were observed in T1-RX. Namely, the dislocation density in T1-RX was radically lower than that in T1-SR. It should be noted here that small dots observed in both of Fig. 5(a) and (b) at comparable density were not the dislocations formed by the rolling but the defects induced by the ion milling. Therefore, it was concluded that the growth rate of W_2C was dependent on dislocation density under the present conditions, and the reduction in W_2C growth rate by recrystallization is due to decrease in dislocation density. The correlation between W_2C growth rate and hardness could also be understood by taking account of a generally-observed relationship that the reduction in dislocation density leads to that in hardness. The dislocations are considered to act as diffusion paths of carbon and nucleation sites of carbide. Further investigation is, however, necessary to clarify the mechanism underlying the enhancement of carburization by dislocations.

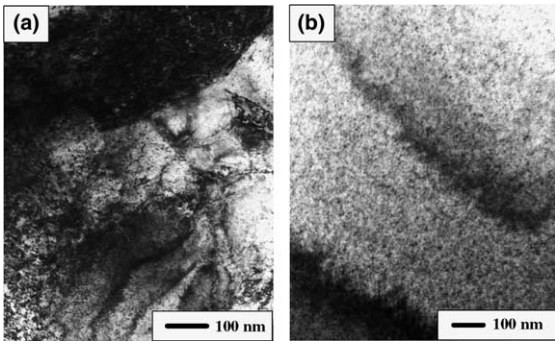

Fig. 5. Bright field images of T1-SR (a) and T1-RX (b).

As mentioned in Section 1, Yeh et al. [10] examined the reaction between tungsten thin films and diamond substrates and reported that the grain boundary diffusion of carbon in tungsten plays an important role in the reaction. On the other hand, in the present study, no significant influence of the grain boundary density was observed on W_2C growth rate as described above. This difference can be ascribed to the difference in the grain size. In the tungsten thin films prepared by Yeh et al. [10], the grain size was very small and less than 100 nm. On the other hand, the grain sizes in the present specimens were considerably larger as shown in Fig. 1. In the case of T1-RX, the sizes of most grains were in a range from 5 to 40 μm. The determination of grain size was difficult for the specimens with SR annealing because the elongated grains had high aspect ratios. The distance between grain boundaries, however, appears to be the order of several μm in Fig. 1(b). Namely, the density of grain boundaries in the tungsten films prepared by Yeh et al. [10] was remarkably higher than that in the present specimens. Such high density of grain boundaries appears to be a cause of significant contributions of grain boundaries in carburization process. In other words, both of grain boundary and dislocation can enhance the growth of carbides, and the ratio in their densities would determine which type of the defect plays a dominant role. Accordingly, it is expected, in principle, that hardness can be used as a measure to predict the growth rate of carbides, because both of the increase in dislocation density and the decrease in grain size lead to increase in hardness. The deformation process during hardness measurement, however, is complicated, and hence careful examinations are necessary to obtain the quantitative correlation between hardness and growth rate of carbides.

4. Conclusions

The solid state reaction between amorphous carbon films and tungsten sheets prepared under different rolling and heat treatment conditions were examined at 1073 K, and the following conclusions were derived:

(1) The carbide formed was W_2C, and no peak of WC was observed in X-ray diffraction patterns.
(2) The grain boundary density on the surface of substrate tungsten had no considerable influence on the growth rate of W_2C.
(3) The growth rate of W_2C was significantly reduced by recrystallization as well as dislocation density.
(4) Dislocation density was a key factor to determine the growth rate of W_2C under present conditions.

Acknowledgments

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