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Journal of Nuclear Materials 258–263 (1998) 896–901

journal of nuclear materials

Hydrogen retention in high-Z materials with various contents of carbon

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Abstract

In order to estimate hydrogen retention and recycling in high-Z plasma facing components, bulk hydrogen retention in molybdenum and tungsten co-existing with carbon has been studied. Hydrogen retention in powdered specimens of molybdenum and tungsten is considerably higher than that in sheet specimens due to surface impurities and defects. When molybdenum and tungsten are well carbonized, bulk hydrogen retention is drastically reduced. Coexisting carbon strongly suppresses hydrogen diffusion to reduce absorption rate into the specimen. Ion and neutron irradiation may produce free carbon to enhance the hydrogen retention in molybdenum and tungsten.

1. Introduction

Applicability of high-Z materials is of current interest for plasma facing components such as divertor targets in the next fusion experimental reactor. Especially, molybdenum and tungsten are very attractive due to their low erosion yield and excellent thermo-physical properties [1–4]. Because of their low hydrogen solubility these materials are also expected to show low tritium retention and recycling rates [5,6]. In ITER, however, high-Z components will be used together with carbon materials [7,8], and most probably carbonized at high temperatures. Furthermore, installation of tungsten-coated graphite tiles has been already tested in other devices, such as ASDEX Upgrade [9]. Although hydrogen solubility in the stoichiometric carbides Mo_2C and WC is believed to be very low, the codeposited carbon layer on these materials may have a rather high hydrogen retention in analogy to the codeposited layer of berylium on graphite in JET where H/(C+Be) was found very similar to H/C [10]. In the recent years, various authors vigorously examined hydrogen retention in tungsten and molybdenum using ion implantation and plasma exposure [11–20]. In order to estimate hydrogen retention and recycling in plasma facing components it is strongly required to obtain data not only on the retention within a near-surface region but also on bulk retention. In the present study, hydrogen absorption into molybdenum and tungsten coexisting with (or containing) carbon has been examined to obtain fundamental data on hydrogen bulk retention in high-Z plasma facing components coexisting with carbon.

2. Experimental

Raw materials of this study are molybdenum and tungsten powder (~50 μm in diameter) with a purity of 99.9%. After mixing these materials with pyrolytic carbon (Pyroid, Pfizer Inc.) ground into powder (~80 μm in diameter), they were molded in the form of a slurry with the addition of ethyl alcohol. Followed by vacuum drying, test specimens were produced by heating them in a temperature range of 1000–1550°C for 2 h in vacuum below 10^{-3} Pa. The change of the structure was characterized by powder X-ray diffraction (XRD) using monochromated CuKα radiation. Measurements of hydrogen retention were performed at 1000°C under a hydrogen atmosphere of approximately 10 kPa in a constant volume in an appratus described in detail

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PII: S0022-3115(98)00311-0

elsewhere [21]. The amount of retained hydrogen (retention) was evaluated from the pressure change of the system monitored by a Capacitance Manometer (Baratron 390H, MKS Inc.).

3. Results and discussion

3.1. Tungsten and its carbides

Hydrogen absorption tests were performed for the mixtures of tungsten and carbon annealed at 1500°C. Fig. 1 shows the results measured at a hydrogen pressure of 10 kPa. Bulk hydrogen retention in carbon (Pyriod) in the same conditions was 280 ppm at H/C atomic ratio, which is larger than those for isotropic graphites such as ISO-880U (201 ppm) and AXF-5Q1 (157 ppm) [22]. Because of the rather poor degree of graphitization of Pyroid (11.7%), the high retention is consistent with the correlation between hydrogen bulk retention and the degree of graphitization in the previous work [22]. Hydrogen retention in the original tungsten powder shows a significantly higher value (52.3 ppm) than previously reported hydrogen solubilities such as 0.02 ppm [23] and 0.28 ppm [24]. The values of hydrogen solubility for tungsten are widely scattered between each datum reported by various authors. It is believed that the hydrogen solubility in tungsten is very sensitive to impurities (e.g. carbon and oxygen), defects and its structures [5,6,25]. Such effects of impurity and structure have been also reported on hydrogen inventory and release from ion implanted tungsten [12,16,17]. In our case, impurity effects directly caused by oxygen atoms can be excluded as a reason of high hydrogen retention, since we could not observe any difference in hydrogen absorption for the sample previously annealed in hydrogen atmosphere to remove oxides. Therefore, the large deviation between the reported hydrogen solubility and the hydrogen retention obtained in this study can be ascribed to the powder form of our specimens, which have quite a large surface area having a possibility to be covered up with impurity carbon. In fact, hydrogen retention measured for a tungsten sheet (thickness: 0.5 mm) was extremely low (Fig. 1), and with approximately 1 ppm close to the detection limit of the measuring system. The mixtures of tungsten and carbon sintered together show intermediate values of hydrogen retention, and the values have a tendency to increase with the content of carbon (Fig. 1). Since the stoichiometric carbide of WC is expected to have low hydrogen retention, WC material from the market in a powder form (99.9%, Kishida Chemical Co. Ltd.) has been examined. The retention obtained was only 1.7 ppm at H/(W + C). This suggests that the annealing conditions applied in this study, which are 1500°C and 2 h, are not sufficient to fully carbonize the mixtures of tungsten and carbon.

In order to confirm the formation of carbides with the combination of tungsten and carbon, the structures of the specimens before and after vacuum annealing (1000–1550°C) were determined by XRD. Fig. 2 which shows the XRD patterns proves that tungsten and carbon react to produce W_2C and WC above 1200°C. However, even after the annealing at 1550°C for 2 h, only 60% of the initial tungsten was carbonized, and some carbon and metallic tungsten remained as shown

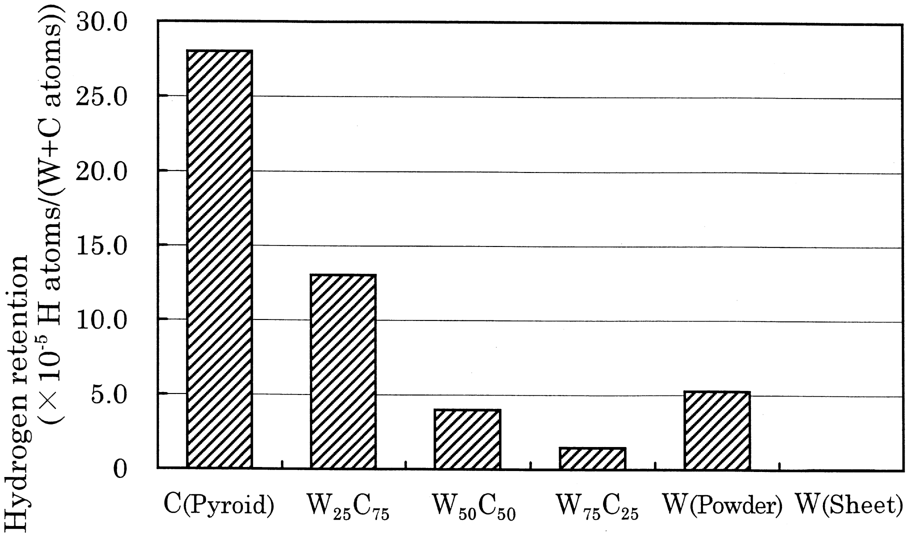

Fig. 1. Hydrogen retention measured for the mixtures of carbon and tungsten previously annealed at 1500°C for 2 h (temperature: 1000°C, hydrogen pressure: 10 kPa).

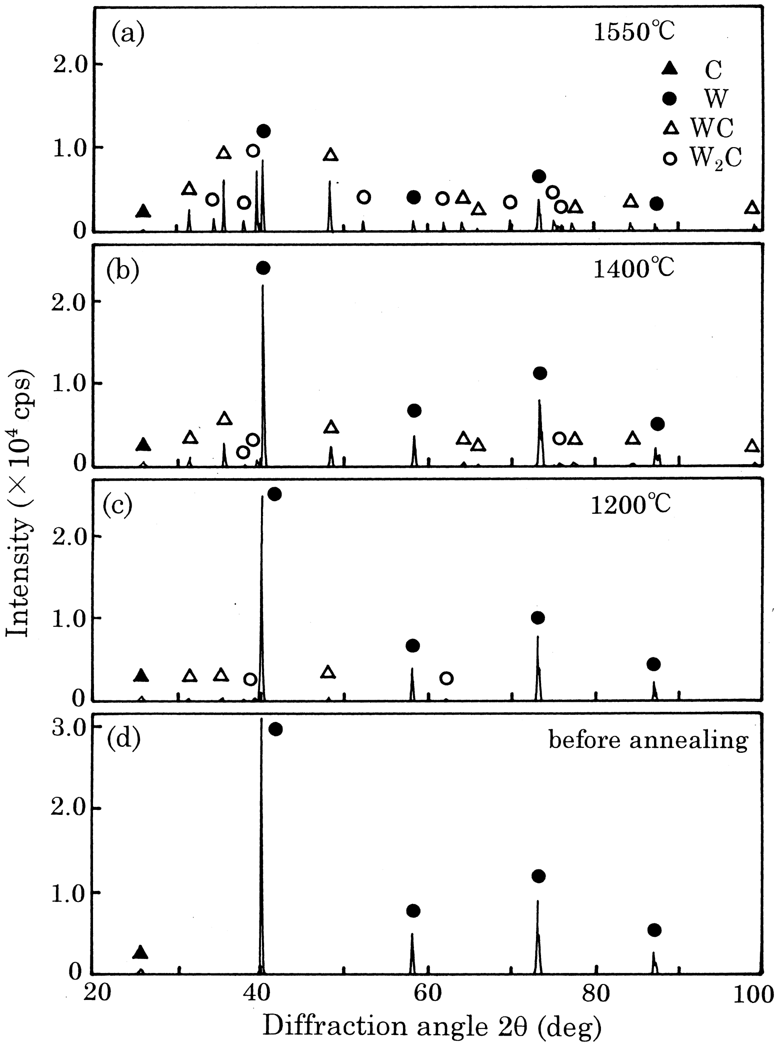

Fig. 2. The XRD patterns of the mixtures of carbon and tungsten before and after annealing at various temperatures for 2 h.

in the XRD patterns (Fig. 2(a)). Hydrogen retention was measured also for these specimens annealed at various temperatures. The relation between the hydrogen retention and the ratios of formed carbide is given in Fig. 3. One can observe the hydrogen retention decreasing with the progression of carbide formation, and fully reacted carbide shows quite low hydrogen retention. For these reasons, the hydrogen bulk retention shown in Fig. 1 should be ascribed to the hydrogen absorption into unreacted carbon and to the hydrogen trapped in micropores of the tungsten–carbon mixture. Hence, tungsten coexisting with carbon has low bulk hydrogen retention if it is converted into well-reacted carbides. This suggests that the dangling carbon bonds, which play a role of hydrogen trapping sites, would disappear by forming bonds with tungsten atoms. However, the possibility that carbon impurities in tungsten (or on the surface of tungsten) lead to a drastic increase in hydrogen retention cannot be denied, since the hydrogen retention in tungsten powders is 50 times as large as that of tungsten sheet. In fact, Wang et al. [20] have reported that carbon impurities strongly increased the hydrogen inventory in ion implanted tungsten samples. This shows that ion irradiation produces active carbon atoms from the stable state of W–C bonds leading to very high hydrogen retention. For the same reason, an increase of hydrogen inventory may take place for neutron irradiated tungsten carbide.

3.2. Molybdenum and its carbides

Molybdenum could be converted into nearly its stoichiometric carbide, Mo$_2$C, by annealing at 1500°C for 2 h, whereas only 36% of tungsten was carbonized (WC

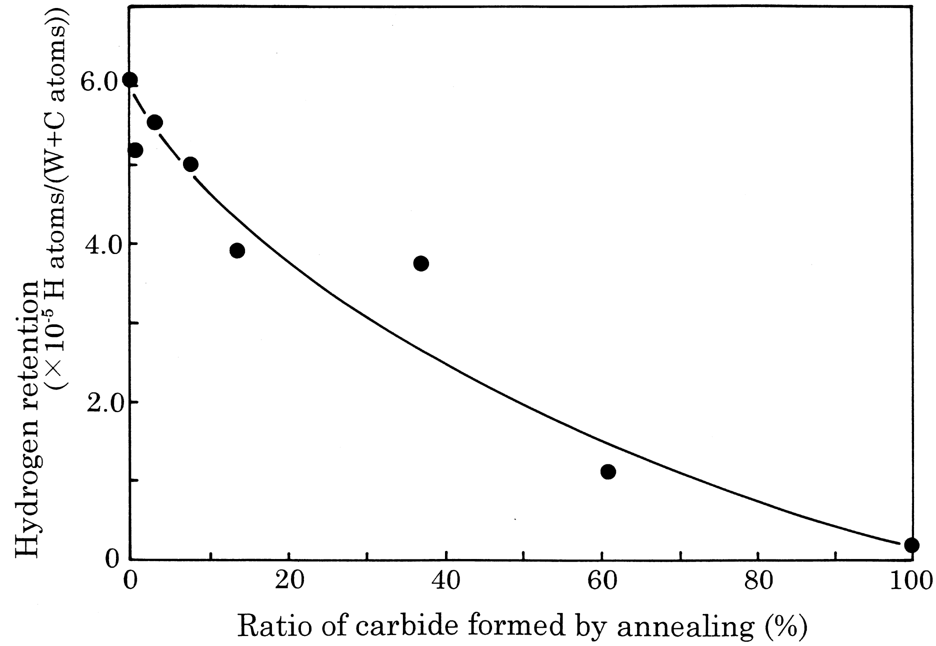

Fig. 3. Hydrogen retention measured for $W_{50}C_{50}$ previously annealed in the temperature range of 1000–1550°C for 2 h. The line is a guide to the eyes (temperature: 1000°C, hydrogen pressure: 10 kPa).

and W_2C) for the combination of tungsten and carbon at the same conditions. The bulk hydrogen retention obtained is shown in Fig. 4. The retention in metallic molybdenum shows a high value (150 ppm) similar to that for tungsten, while the reported solubility is rather low (e.g. 10.5 ppm [26], 15.9 ppm [27] and 99 ppm [28]). Also in the case of molybdenum, the effect of impurities and structure on the change of hydrogen solubility has been pointed out [5,6,29]. In contrast to powder molybdenum, a molybdenum sheet (thickness: 0.5 mm) showed rather low hydrogen retention of 23 ppm at H/Mo, which is close to the reported solubility. As shown here, bulk hydrogen retention in molybdenum is higher than in tungsten, while the surface hydrogen retention

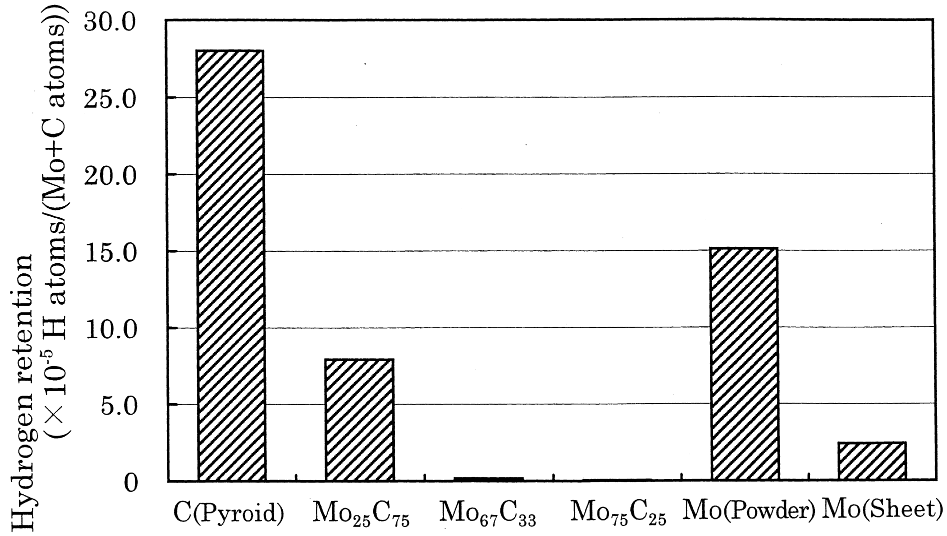

Fig. 4. Hydrogen retention measured for the mixtures of carbon and molybdenum previously annealed at 1500°C for 2 h (temperature: 1000°C, hydrogen pressure: 10 kPa).

after ion implantation is opposite [19]. The mixtures of molybdenum and carbon retain smaller amounts of hydrogen compared with their raw materials which are metallic molybdenum and carbon (Pyroid). The specimens of the composition corresponding to the stoichiometric compound, Mo_2C, and lower content of carbon, have significantly low levels of hydrogen retention (1.8 ppm) and below 1 ppm in $Mo_{67}C_{33}$ and $Mo_{75}C_{25}$, respectively. Mo_2C material from the market in the powder form also showed low hydrogen retention (below 1 ppm). On the other hand, excess carbon results in higher hydrogen retention due to the hydrogen absorption by unreacted carbon in the mixture. Hence, molybdenum coexisting with carbon has also a low bulk hydrogen retention when it is sufficiently carbonized. However, carbon impurities in molybdenum will possibly increase hydrogen retention.

3.3. Hydrogen absorption rate

Hydrogen absorption rate constants were determined from the pressure decrease of the measuring system [30]. Typical results obtained for the mixtures of carbon and tungsten are given in Fig. 5. In these results, the absorption rate constant of $W_{25}C_{75}$ is the smallest of all the specimens, suggesting that hydrogen absorption is strongly suppressed. In comparison with the absorption rate constants for carbon (Pyroid) and metallic tungsten, one can observe that the constants are not so much different in spite of the great difference between their diffusion coefficients (i.e graphite: 7.6×10^{-16} m^2/s [31], tungsten: 1.05×10^{-8} m^2/s [23] (at 1000°C)). In the absorption measurement of sheet tungsten, the rate constant was 4×10^{-3} s^{-1}, and the diffusion coefficient can be calculated to be approximately 1.0×10^{-9} m^2/s. Consequently, we can conclude that hydrogen absorption into tungsten in a powder form, which may be accompanied with impurity covering up or surface contamination, is suppressed to reduce the rate constant.

4. Conclusions

Bulk hydrogen retention in molybdenum and tungsten coexisting with carbon was studied. The results obtained in the present study are summarized as follows.

(1) Hydrogen retention in powdered specimens of molybdenum and tungsten were considerably higher than that of sheet specimens (tungsten: 50 times, molybdenum: 7 times). This can be ascribed to the high sensitivity of these metals on hydrogen trapping caused by impurity, defects and their structures.

(2) Tungsten was partly carbonized into W_2C and WC by vacuum annealing above 1200°C with carbon. Also the metallic form remained 40% even at 1550°C, while molybdenum entirely carbonized into Mo_2C at 1500°C.

(3) When molybdenum and tungsten are well carbonized, hydrogen retention was drastically reduced by the formation of stable Mo–C and W–C bonds. Mo_2C and WC showed 1 ppm (or below) and 1.7 ppm at 1000°C under 10 kPa of hydrogen, respectively.

(4) Hydrogen absorption into tungsten was strongly suppressed by the formation of carbide, and the rate constant became smaller.

(5) When high-Z components in a fusion device keep clean surfaces and structural integrity, bulk hydrogen retention will be low. However, if they are contaminated

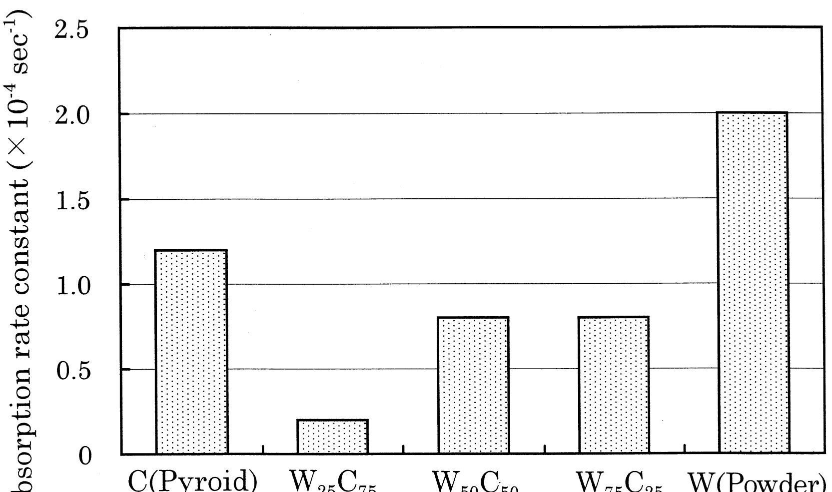

Fig. 5. Absorption rate constants estimated from hydrogen retention measurements for the combination of carbon and tungsten at 1000°C under a hydrogen pressure of 10 kPa.

with carbon impurities, retention will be increased. Ion irradiation or neutron irradiation will enhance the retention to a level similar to that of carbon and graphite by the appearance of active free carbons.

Acknowledgements

This work was supported by a Grant-in-aid for scientific research of the Ministry of Education (Japan).

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