



Damage process of resolidified part on CVD-W coated molybdenum under high heat load

S. Tamura ^{a,*}, K. Tokunaga ^b, N. Yoshida ^b

^a *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

^b *Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

Abstract

In view of the recent interest in high-Z metals as plasma facing materials, a high purity CVD-W (99.99998%) coated molybdenum material was prepared. The specimens had been melted at the joint interface under high heat load were made in order to prove the change. Then heat load experiments were performed on these specimens using an electron beam. As the results, the formation of the W–Mo alloy on the heat-affected surface leads the significant weight loss in the temperature range around 2500 °C. But in the temperature range around 2000 °C, the weight loss did not occur. In this experiment, we also carried out a research into the diffusion behavior of a high purity CVD-W/Mo system. These results indicated that the thermal and adhesion properties between the molybdenum substrate and the high purity CVD-W coating were good under high heat loads.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: CVD tungsten; Molybdenum; Tungsten coating; Heat load; Diffusion coefficient; Damage process

1. Introduction

Tungsten and its alloys are considered as potential candidate materials for high heat flux components such as limiter blocks and divertor tiles in fusion experimental devices because of their good thermal properties and the low sputtering yield [1,2]. However, tungsten has the disadvantages of brittleness below 400 °C and of heaviness. In order to overcome its disadvantages, the thin tungsten coating on light and ductile materials with high melting point such as carbon materials and molybdenum are considered as advanced high heat flux materials [3,4].

On the other hand, we have large experience of molybdenum limiters in TRIAM-1 and TRIAM-1M [5]. For example, the surfaces of molybdenum limiters facing to the electron drift side suffered very severe damage

such as melting and cracking by the unexpected high heat flux during the challenging discharge experiments and mis-controlled discharges [6]. The evaporated molybdenum atoms not only contaminated the plasma but also changed the properties of the plasma facing wall by depositing on it. It is an important issue to reduce the evaporation from the limiters for the high power steady-state operation. One of the ways to suppress the evaporation from the material side is the deposition of tungsten, which has much higher melting point and lower vapor pressure, on the molybdenum limiter. In the present study, we prepared tungsten-coated molybdenum specimens by a chemical vapor deposition (CVD) method and examined their thermal behavior under high heat loads. As reported in Ref. [7], this material showed good heat load resistance up to 1800 °C. It is very important for the limiters in the experimental apparatus that they can keep reasonable properties even after the unexpected severe heat loads which may cause melting and cracking. In the present experiment, therefore, we focused on the metallurgical change of the interface and the thermal behavior of the melted and resolidified parts.

* Corresponding author. Tel.: +81-92 583 7719; fax: +81-92 583 7690.

E-mail address: tamura@riam.kyushu-u.ac.jp (S. Tamura).

2. Experimental

2.1. Specimens

Samples of very pure tungsten (99.99998%) deposited on powder metallurgy (PM) molybdenum substrates were produced by Tokyo Tungsten Co., Ltd. [8]. Thicknesses of the tungsten coating and the molybdenum substrate were 1 and 5 mm, respectively. The CVD-W/Mo samples were cut out pieces of 10 mm × 10 mm × 6 mm, and then were treated for one hour at 1000 °C in a vacuum to stabilize the microstructure.

2.2. Heat load

The specimens were heated with a uniform electron beam by using the electron beam irradiation test simulator at Research Institute for Applied Mechanics, Kyushu University [9]. The energy of the electron beam was 20 keV and its current was adjusted to obtain the desired temperature. Heat load tests for 60 s were repeated for four different specimens with and without pre-resolidification and different peak temperatures. Details of the heat load conditions are summarized in Table 1. The resolidified parts on the tungsten coating were formed by focusing the electron beam.

The specimens were just put on a horizontal holder made of Ta to reduce thermal contact. The surface temperature of the specimen was measured with two-color optical pyrometers (450–1100 °C, 1100–3100 °C). The surface morphology and the internal structure were observed by a scanning electron microscopy (SEM). The compositional change before and after the heat loads was examined by an energy dispersion X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Modification of resolidified parts of the CVD-W coating

Resolidified part was made at first by heating up to 2620 °C for about 2 s and the cyclic heat load test was

performed successively. As shown in Fig. 1(a), the resolidified surface was rather smooth and remarkable cracks were not formed. In the part, however, alloying of tungsten and substrate material (molybdenum) occurred. The contents of molybdenum and tungsten estimated by EDS were about 74 at.% and 26 at.%, respectively. During the cyclic heat load test up to 2500 °C, the structure and the chemical composition at the resolidified part changed significantly (see Fig. 1). By repeating the pulse heating up to 2500 °C, a fine uneven structure and cracks appeared at the surface. The cracks expanded and their width reached about 40 μm after repeating 10 pulse heatings. It is worth to note that the preferential sublimation of the molybdenum occurred and the molybdenum content at the surface decreased to 22 at.% after the 10 pulse heatings.

An element Mo, which was contained at the bottom of these cracks, was richer than that of the structures (56 at.%W–44 at.%Mo). These results of the structural change are illustrated in Fig. 1(b)–(d). To confirm the observed remarkable sublimation of molybdenum, the emission rate of molybdenum for the temperature history of the specimen no. 1 was estimated by using Langmuir's evaporation equation (see Fig. 2). It is clear that remarkable emission of molybdenum atoms occurred above 2300 °C.

Fig. 3 shows the side view of the specimen no.1 before and after the cyclic heat load, up to 2500 °C. Formation of a large step of about 10 μm indicates that the strong evaporation occurred at the molybdenum interface. On the other hand, the fine uneven structures were also observed at the expanded tungsten/molybdenum interface, which was formed by the mutual diffusion of tungsten and molybdenum. These results indicate that the fine uneven structures were formed by the selective sublimation of molybdenum from the alloyed area.

The fine uneven structures on the resolidified parts were given excessive heat. Extractions of the hotspots were observed with the naked eye during irradiation.

Fig. 4 shows the proportions of the total weight loss of the specimens after heat load tests. The weight loss of the specimen no. 1 was caused by sublimation of Mo from the un-coated surface of molybdenum substrate. After the heat load tests of 10 shots, the weight loss of

Table 1
The experimental conditions of cyclic electron beam irradiation

Specimen	Size of the resolidified part on the CVD-W coating (mm ²)	Initial weight (g)	Peak temperature (°C)	Heta flux (MW/m ²)
No. 1	–	6.2274	2500	3.7
No. 2	3	6.2190	2500	3.7
No. 3	–	6.3405	2000	2.8
No. 4	85	6.5953	2000	2.8

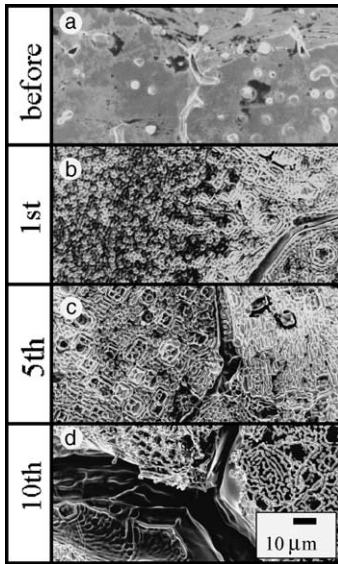


Fig. 1. SEM micrographs of the resolidified part before and after heat load test (the surface temperature: 2500 °C).

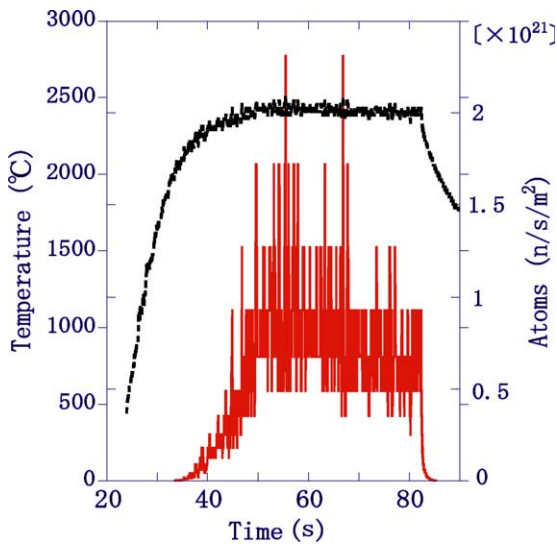


Fig. 2. Relations between sample temperature and emission of Mo atoms.

the specimen no. 2 was 28.5 mg. It was about 3.5 times that of the specimen no. 1. In addition to the sublimation of Mo, the extraction of the fine uneven structures which were heated excessively led the specimen no. 2 to the significant reduction of its weight. On the other hand, the weight loss of the specimen no. 4 (peak temperature 2000 °C) which had had a resolidified part did not occur by the heat load tests of 10 shots at each peak temperature around 2000 °C. The fine uneven structures

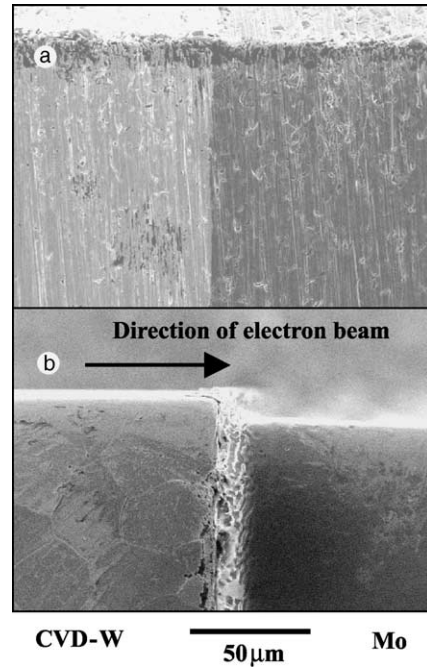


Fig. 3. Side views of the specimen (a) before and (b) after cyclic heat load (2500 °C) of 10 shots.

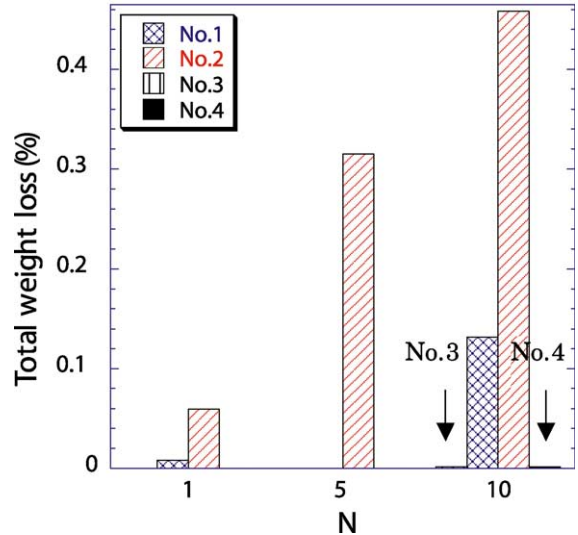


Fig. 4. Total weight loss as a function of shot number.

like that of the specimen no. 2 were not formed on the resolidified part of the specimen no. 4.

3.2. Mutual diffusion at the joint interface

Annealing experiments were also performed on the CVD-W coated molybdenum material to investigate the

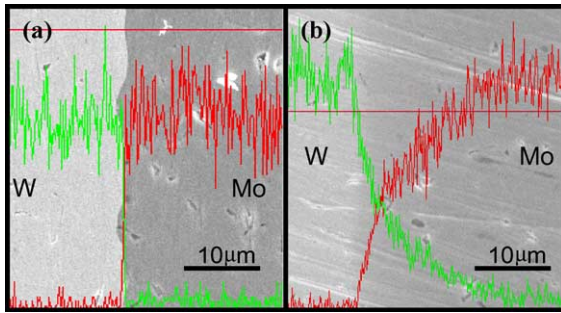


Fig. 5. The SEM images of CVD-W/Mo and the line distributions of elements W and Mo in the thickness direction (a) before and (b) after annealing for 1520 s at 2500 °C. (polished with #2000).

diffusion behavior at the joint interface. According to EDS line analysis in the joint interface of the coating which reached above 1800 °C, a W–Mo diffusion layer was formed. The thickness of this diffusion layer increased with increasing its temperature. A continuous series of solid solution occurs between Mo and W at all temperature. There is no trend to form brittle compounds between the two metals [10]. These results indicate that diffusion at the joint interface contributes to the enhancement of the adhesion property.

Fig. 5 shows the line distribution images of elements W and Mo in the thickness direction at the joint interface of this coating material. This result indicates that the molybdenum substrate dissolves tungsten coating. That is, mobility of Mo atom was larger than that of W atom. But Kirkendall voids were not observed at around the joint interface in these heating conditions. In this experiment, we obtained the mutual diffusion coefficient of Mo atoms in the high purity CVD-W/Mo system. The Boltzmann–Matano analysis was employed for the determination of diffusion coefficient. These results were shown in Fig. 6. These diffusion coefficients changed exponentially at all concentration of Mo. But, Bewlay et al. [11] reported that up to a Mo concentration of ~50 at.% in the potassium (70 wtppm) doped W, the diffusion coefficient did not change significantly. These results lead us to the conclusion that high purity CVD-W suppresses the diffusivity of Mo atoms.

Fig. 7 shows the reduction of the CVD-W thickness as a function of incubation time in the temperature range about 2500 °C. the reduction of thickness is directly proportional to the square root of the incubation time. Life of this coating material in this temperature range can be determined by its proportionality constant $0.147 \mu\text{m}/\text{s}^{1/2}$. This reduction rate is very small to keep the effectiveness of the 1mm thick coating in the temperature range about 2500 °C.

In view of ‘consumption’ of such coating materials in the fusion experimental devices, there is a thing that felt

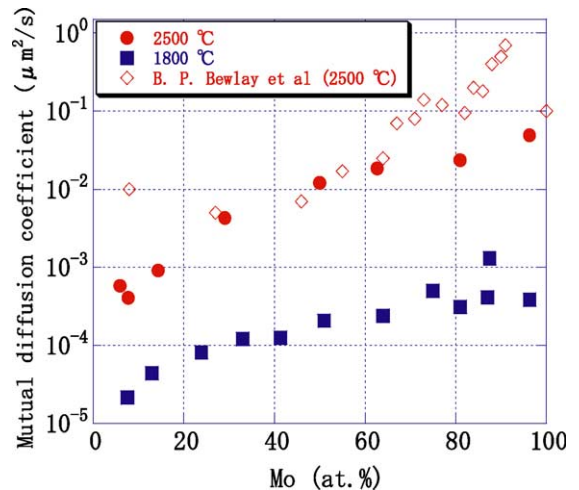


Fig. 6. Mutual diffusion coefficient vs. Mo concentration for CVD-W coated molybdenum specimens annealed at two temperatures.

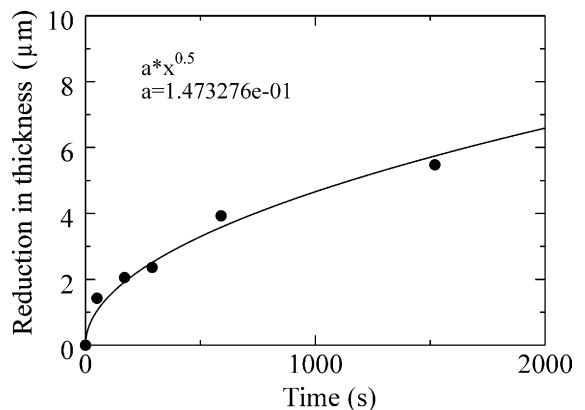


Fig. 7. Reduction of the coating thickness as a function of incubation time in the temperature range 2500 °C.

uneasy; it is ‘corrosion’ of the coated tungsten by the cooperative effect of co-deposition [12,13] and heat loads. For example, after Mo were deposited on the coated tungsten surface, the formation of the W–Mo alloys are enhanced by heating the co-deposited region up to the temperature of above 1800 °C. If these alloyed regions were heated up to over 2300 °C, the fine uneven structures of the W rich would be formed by sublimation of Mo. These fine uneven structures are increased absorption of kinetic energy of the incident particles, because these structures prevent the reflection of them. Essentially, these fine uneven structures are apt to be heated violently because they have one- or two-dimensional thermal conductive property. For these reasons, the structures are extracted from these alloyed regions.

It is predicted that these processes cause erosion of the tungsten walls.

4. Conclusions

Experiments have been performed to prove the suitability and the load limit of CVD-W coated materials.

- (1) Formation of the W–Mo alloy on the heat-affected surface leads the significant weight loss in the temperature range over 2300 °C. But from the view point of effectiveness of the tungsten coating, the CVD-W coating prevents erosion of the molybdenum substrate in the temperature range from 2300 to 2500 °C.
- (2) W–Mo diffusion layer was formed at the joint interface of the coating above 1800 °C. It is suggested that the formation of the diffusion layer contribute to the enhancement of the adhesion property.
- (3) The reduction rate of coating thickness is very small to keep the effectiveness of the 1 mm thick coating in the temperature range about 2500 °C.
- (4) To suppress the formation of the W–Mo alloy on the tungsten-coating surface, all the places should be coated with CVD-tungsten, because they are as sources of the Mo deposition in fusion experimental devices.

References

- [1] N. Yoshida, *J. Nucl. Mater.* 266–269 (1999) 197.
- [2] K. Sato, K. Nakamura, S. Suzuki, M. Araki, M. Dairaku, K. Yokoyama, M. Akiba, *Fusion Technol.* 30 (1996) 769.
- [3] G. Maddaluno, F. Pierdominici, M. Vittori, *J. Nucl. Mater.* 241–243 (1992) 908.
- [4] W. Hohenaure, H. Bolt, J. Linke, W.K.W.M. Mallener, *Fusion Technol.* 34 (1997) 18.
- [5] K. Tokunaga, T. Fujiwara, S. Fukuda, T. Muroga, N. Yoshida, *J. Nucl. Sci. Technol.* 27 (4) (1990) 333.
- [6] N. Yoshida, K. Tokunaga, T. Fujiwara, K. Tawara, T. Muroga, S. Itoh, TRIAM-group, *J. Nucl. Mater.* 196–198 (1992) 415.
- [7] S. Tamura, K. Tokunaga, N. Yoshida, *Proceedings ICFRM-10*, 14–19 October 2001, Baden-Baden, Germany.
- [8] T. Hayashi, S. Takaoka, A. Ichida, T. Igarashi, H. Ohara, T. Yoshioka, M. Miyake, *TOTAN Tech. Rev.* (4) (1993) 1.
- [9] K. Tokunaga, K. Matsumoto, Y. Miyamoto, N. Yoshida, *J. Nucl. Mater.* 212–215 (1994) 1323.
- [10] L.M. Zhang, H.P. Xiong, L.D. Chen, T. Hirai, *J. Mater. Sci. Lett.* 19 (2000) 955.
- [11] B.P. Bewlay, C.L. Briant, M.L. Murray, *Metall. Trans. A* 12 (1998) 2933.
- [12] T. Hirai, T. Fujiwara, K. Tokunaga, N. Yoshida, S. Itoh, A. Komori, O. Motojima, *J. Nucl. Mater.* 283–287 (2000) 1177.
- [13] N. Yoshida, T. Hirai, K. Tokunaga, S. Itoh, *J. Nucl. Mater.* 290–293 (2001) 1030.