ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 1177–1181

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Structure of materials deposited on the plasma facing surface in TRIAM-1M tokamak and the effect on hydrogen recycling

T. Hirai [a,*], T. Fujiwara [a], K. Tokunaga [a], N. Yoshida [a], A. Komori [b], O. Motojima [b], S. Itoh [a], TRIAM group

[a] *Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasugakoen, Kasuga Fukuoka 816-8580, Japan*
[b] *National Institute for Fusion Science, Oroshi, Toki, Gifu 509-5292, Japan*

Abstract

Microstructure and chemical composition of depositions in TRIAM-1M under long pulse discharges have been examined. It is found that the deposition has a defective structure; the grain size is approximately 1 nm and the crystalline structure is not the normal body centered cubic (bcc) but is a face centered cubic (fcc). By comparing with the vacuum-deposited molybdenum in various conditions, it is concluded that co-deposited oxygen plays an essential role for the defective structure. The vacuum-deposited molybdenum, which has the same structure as the depositions in TRIAM-1M, shows very large and strong hydrogen retention. Implanted deuteriums are desorbed as D_2, DH, D_2O and DHO. The present work indicates that re-deposition of sputtered atoms on plasma facing surfaces will be a serious problem even in a metallic tokamak. More attention should be paid to hydrogen retention in the deposited material. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Impurities emitted from the surfaces of in-vessel components due to plasma wall interaction re-deposit on the surface. Consequently the surfaces are covered with mixtures of all elements from the in-vessel components. Such deposition-dominant surfaces have been observed in many tokamaks [1–7]. In carbon dominant devices, co-deposition of carbon with hydrogen isotopes has been observed [2–4]. Due to the deposition, the surface of the vessel wall materials are largely modified with respect to chemical composition and microstructure. Moreover, the modification may change the physical properties of materials, especially hydrogen retention properties, and have a great impact on hydrogen recycling under a long pulse operation.

In the present work, the chemical composition and microstructure of depositions in TRIAM-1M [8] have been studied, and the formation mechanism of the depositions and the influence on hydrogen retention have been examined.

2. Experiments

TRIAM-1M is a high field tokamak with superconducting toroidal field coils. To obtain the deposition, pre-thinned tungsten and 304 stainless steel (SS) specimens fixed on the surface probe system [9] were exposed to the discharges in the scrape-off layer (SOL) in 1997. The duration of each discharge was about 1 min and the total reached 31.5 min. Typical plasma parameters such as plasma current (I_P), electron density ($\bar{n}_e$), ion temperature (T_i) were 20–25 kA, $\sim 2 \times 10^{12}$ cm^{-3}, 1.5–2.5 keV, respectively. After exposing to plasmas, the chemical composition and microstructure of the specimens were examined by means of energy dispersive spectrometry (EDS), Rutherford backscattering spectrometry (RBS), and transmission electron microscopy (TEM).

In addition, vacuum-depositions of molybdenum were carried out in various conditions in order to

---

[*] Corresponding author. Present address: Forschungszentrum Jülich, Institut für Plasmaphysik, D-52425 Jülich, Germany. Tel.: +49-2461 61 2183; fax: +49-2461 61 2660.

E-mail address: t.hirai@fz-juelich.de (T. Hirai).

0022-3115/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(00)00320-2

simulate the deposition in TRIAM-1M. The substrates were pre-thinned or bulk 304SS specimens. The vacuum-depositions have been carried out in a high-vacuum ($<10^{-4}$ Pa) or low-pressure hydrogen or oxygen atmospheres. The partial pressures of hydrogen were controlled at $P_{H_2} = 10^{-3}$ or 10^{-2} Pa and those of oxygen at $P_{O_2} = 5 \times 10^{-4}$ or 5×10^{-3} Pa during the vacuum depositions. After the vacuum depositions, the pre-thinned specimens were observed by TEM.

Mo-depositions on bulk 304SS were irradiated with 6 keV D_3^+ (supposing the molecules would split into three atoms with the equal energy in specimens, the beam would be 2 keV D^+) ions at room temperature to a fluence of 3×10^{21} ions/m^2. The thickness of the Mo-deposition was about 50 nm, which is greater than the projected range of 2 keV D^+ ions (<30 nm). Hence, the majority of the implanted D ions would accumulate in the Mo-deposition. Desorptions of DH, D_2, DHO and D_2O were measured with a quadrupole mass spectrometer (QMS) under heating with a ramping rate of 1 K/s. Desorption spectra from the bulk specimens of molybdenum (99.95% pure) and 304SS were also obtained as comparison. Desorption rates of DH, D_2, DHO and D_2O were calibrated by using a He leak standard.

3. Results and discussion

3.1. Chemical composition of the deposited material

Fig. 1 shows a typical EDS spectrum from the tungsten specimen exposed to the discharges in November 1997. In the present experiment, elements with Z above 11 can be detected, so oxygen cannot be detected even if it exists. Only molybdenum was detected as a metallic element besides substrate tungsten. This means that the deposition was composed of molybdenum that is element of the limiter and divertor plates. This result is consistent with those since 1996, but different from the results before 1996, where iron, chromium and nickel, the major elements of the vacuum vessel (304SS), had been detected in addition to molybdenum [5–7]. Depositions formed on long term samples installed at the different toroidal positions were also composed of only molybdenum. This indicates that the change of chemical composition on the material probe experiments were not a local phenomenon but global in the torus. Furthermore, recent results from vacuum ultra violet (VUV) spectrometry in TRIAM-1M indicates that the amount of iron impurity emitted into the plasma drastically decreased. One can say that majority of the 304SS surface of the vacuum chamber had been covered with deposited molybdenum.

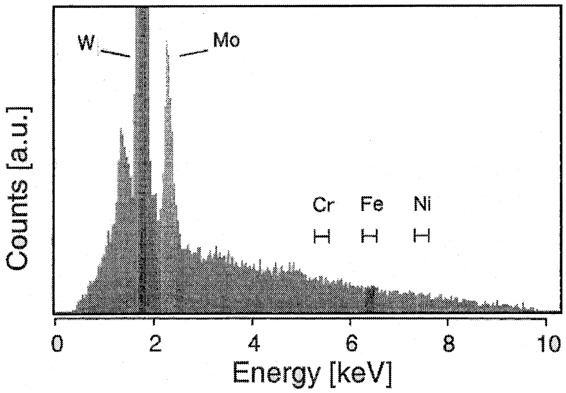

Fig. 1. Typical EDS spectrum of the tungsten specimen exposed to the discharges in November 1997.

3.2. Microstructure of the depositions

Fig. 2 shows electron diffraction patterns and dark field images of microstructures of the deposition on a stainless steel substrate exposed to the discharges. The dark field images were obtained from a part of the diffraction rings. In this imaging condition, only the grains satisfying the Bragg condition have a white contrast [10]. As shown in Fig. 2, the deposition consists of numerous fine grains around 1 nm in diameter. It is important to note that the crystalline structure was not the normal body centered cubic (bcc) but face centered cubic (fcc). One should also note that the structure must be very 'defective', because more than half of the constituent atoms are directly affected by the disordered structure of grain boundaries. To examine the stability of this

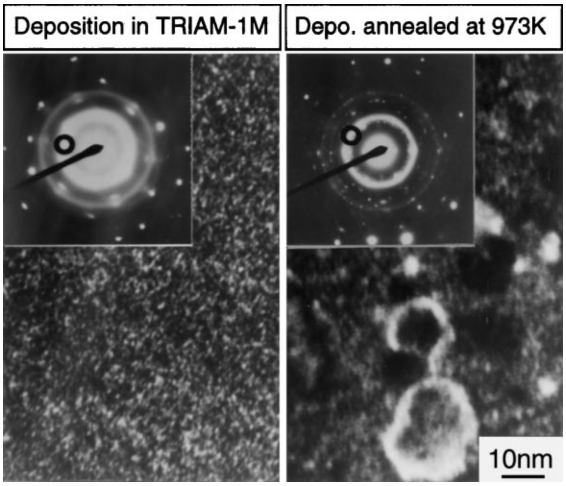

Fig. 2. Electron diffraction patterns and microstructures of the deposition on the stainless steel specimen exposed to the discharges (left) and the deposition annealed at 973 K for 10 min (right). The microstructures are dark field images obtained from a part of the diffraction rings.

defective structure, isochronal annealing was carried out from 373 to 973 K at 100 K steps for 10 min. As a result, it was shown that the fine grains abruptly grew by annealing at 973 K as shown in Fig. 2.

As explained later, co-deposited gaseous atoms such as hydrogen and oxygen may play important roles in formation of the 'defective' deposition in TRIAM-1M. Deposition rates of molybdenum, hydrogen and oxygen were estimated as follows. According to RBS analysis, the total amount of deposited molybdenum was estimated to be 8×10^{21} atoms/m^2. Dividing this by the discharge duration, the mean deposition rate of molybdenum was estimated 4.2×10^{18} atoms/m^{2}s. The flux of hydrogen ions can be derived as 6×10^{21}H-ions/m^{2}s by the following equation [11]:

$$\Gamma_{\text{H-ion}} = n_i C_s = n_i[k(T_i + T_e)/m_i]^{1/2}, \qquad (1)$$

where the n_i is the ion density ($\approx n_e = 10^{17}\,\mathrm{m}^{-3}$), C_s the ion sound velocity, m_i the mass of the hydrogen ion $T_i(\approx T_e)$ the ion temperature, and T_e is the electron temperature (17 eV). One should note that the flux of hydrogen ions is 3 orders of magnitude higher than that of molybdenum. Oxygen is another major gaseous element in the plasma. Although its concentration is less than a few percent of the hydrogen concentration [12], the effects of oxygen may not be negligible because its flux is still one order of magnitude higher than that of molybdenum. This means that molybdenum atoms deposit on a surface covered with adsorbed hydrogen and oxygen, and subsequently stack with the H and O atoms. The gas atoms may prevent free migration of deposited molybdenum atoms and result in the formation of the 'defective' structure.

Fig. 3 shows microstructures and electron diffraction patterns of the vacuum-deposited molybdenum formed in various conditions. The vacuum condition and deposition rate of molybdenum was adjusted to obtain a deposition ratio comparable to the TRIAM-1M case. Depositions formed in a high-vacuum and in a hydrogen atmosphere have a bcc structure with grains 3–10 nm in diameter even if partial pressure is higher. This means hydrogen does not have a strong influence on the structure of the depositions. Depositions formed in an oxygen atmosphere, on the other hand, especially in case of $P_{O_2} = 5 \times 10^{-3}$ Pa, have a similar microstructure to the deposition in TRIAM-1M: namely, an fcc structure with fine grains of about 1 nm in diameter. Moreover, grain growth occurs at the same temperature (973 K) as shown in Fig. 4. These results indicate that oxygen atoms play an essential role in the formation of the deposition in TRIAM-1M. A similar defective structure was observed for vacuum-deposited iron films formed in an oxygen atmosphere [13].

3.3. Deuterium retention in the deposited Mo

Fig. 5 shows thermal desorption spectra of D_2 ($m/e = 4$) and D_2O ($m/e = 20$) obtained from the deuterium-ion-irradiated Mo-depositions formed in an oxygen atmosphere. Data for bulk molybdenum and stainless steel (304SS) are also plotted in the figure for comparison. The retention of implanted deuterium in

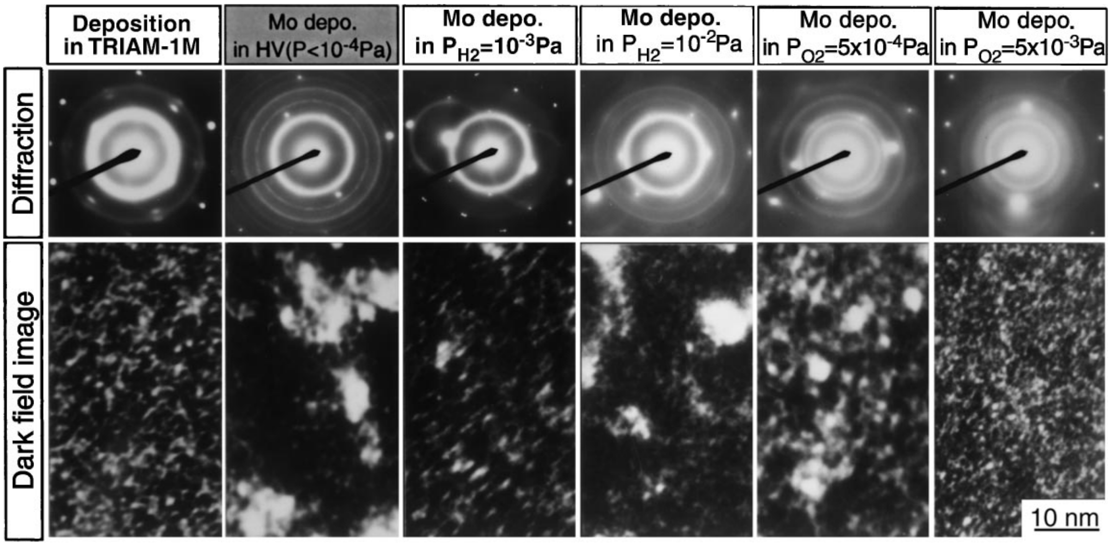

Fig. 3. The microstructures and electron diffraction patterns of the depositions in TRIAM-1M and the vacuum-deposited Mo in various conditions. The left – the deposition in TRIAM-1M; the second left – the Mo-deposition in a high vacuum (<10^{-4} Pa); the middle two – the Mo-deposition in hydrogen atmospheres, $P_{H_2} = 10^{-3}$ Pa and $P_{H_2} = 10^{-2}$ Pa; the second right – the Mo-deposition in oxygen atmospheres, $P_{O_2} = 5 \times 10^{-4}$ Pa and the right – the Mo-deposition in oxygen atmosphere, $P_{O_2} = 5 \times 10^{-3}$ Pa.

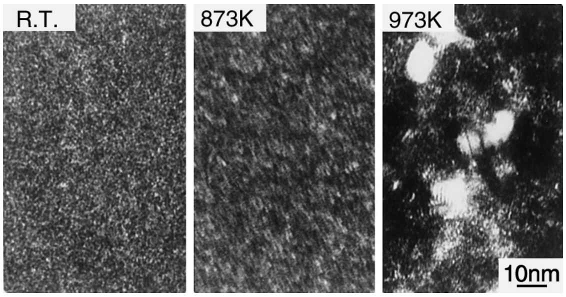

Fig. 4. The microstructure of the Mo-deposition in $P_{O_2} = 5 \times 10^{-3}$ Pa, as deposited and annealed at 873 and 973 K.

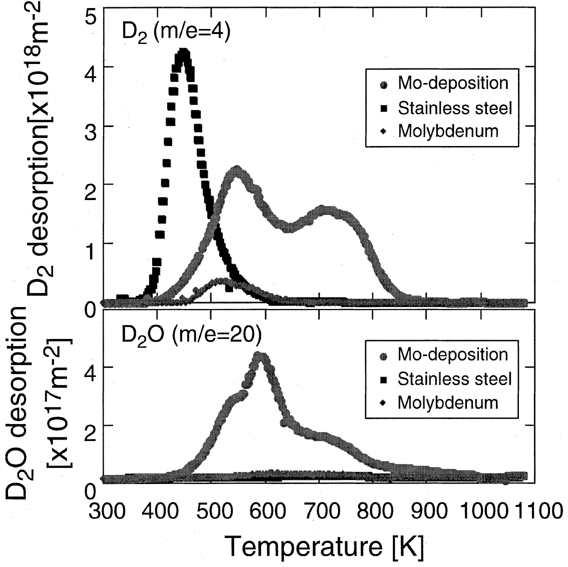

Fig. 5. Thermal desorption spectra of D_2 ($m/e = 4$) and D_2O ($m/e = 20$) obtained from the Mo-deposition in an oxygen atmosphere, molybdenum and stainless steel (SS304) specimens implanted with 6 keV D_3^+ at a fluence 3×10^{21} D/m^2.

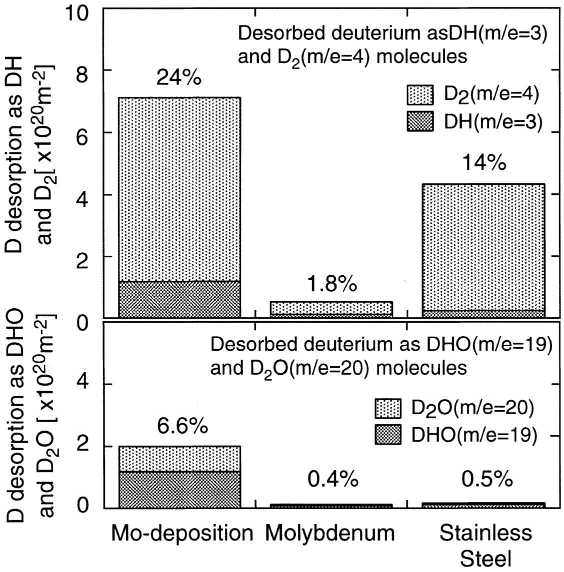

Fig. 6. Retained deuterium in the specimens implanted with 6 keV D_3^+ at a fluence 3×10^{21} D/m^2. The percentage indicates the fraction of the implanted amount.

the deposited molybdenum is much higher and much stronger than in bulk molybdenum. For Mo-deposition, two large desorption peaks of D_2 at around 550 and 720 K are distinguished but only small peaks occur at around 530 K for bulk molybdenum. In the case of D_2O, large desorption occurred only for Mo-deposition. At least four peaks exist above 450 K. Desorption still occurs even at 900 K.

Fig. 6 shows the fraction of the retained deuterium in Mo-deposition, crystalline molybdenum and 304SS for an ion dose of 3×10^{21} ions/m^2. The desorption indicates the total amount of desorbed deuterium as DH, D_2, DHO and D_2O molecules. Only 2.2% of the implanted deuterium is retained in crystalline molybdenum, but 31% is retained in the Mo-deposition. It is also important to note that 6.6% of implanted deuterium is desorbed as water (DHO or D_2O). This supports the interpretation that a large amount of oxygen is trapped in the Mo-deposition in an oxygen atmosphere. Due to its defective structure and trapped oxygen, the metallic deposition can trap large amount of deuterium.

Present work indicates that re-deposition of sputtered atoms on plasma facing surface causes a serious problem such as high retention of hydrogen isotopes in metallic tokamak as well as carbon tokamaks [2–4].

4. Summary

The microstructure and chemical composition of depositions formed in TRIAM-1M have been examined. The major metallic element is molybdenum, which originated from the limiter and divertor plates. Elements of the original vacuum vessel surface, iron, chronium, and nickel, have been not detected. This indicates that the majority of the inner surface of the vacuum vessel was covered with deposited molybdenum.

The depositions have a defective structure; the grain size was about 1 nm and the crystal structure was not the normal bcc but fcc. By comparing with vacuum-deposited molybdenum under various conditions, it was concluded that co-deposited oxygen, which exists in plasma as a residual gas, plays an essential role in the defective structure formation. The molybdenum vacuum deposited in an oxygen atmosphere had the same structure as the deposition in TRIAM-1M, and showed very large and strong deuterium retention. Implanted deuterium was desorbed as D_2, DH, D_2O and DHO molecules.

The present work indicates that re-deposition of sputtered elements on plasma facing surfaces can be a serious problem even in the metallic tokamak.

References

[1] R. Behrisch, M. Mayer, C. Garcia-Rosales, J. Nucl. Mater. 233–237 (1996) 673.

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

[3] K. Krieger, J. Roth, A. Annen, W. Jacob, C.S. Picher, J. Nucl. Mater. 241–243 (1997) 684.

[4] E. Gauthier, A. Grosman, J. Valter, J. Nucl. Mater. 220–222 (1995) 506.

[5] N. Yoshida, K. Tokunaga, T. Fujiwara, K. Tawara, T. Muroga, S. Itoh, the TRIAM group, J. Nucl. Mater. 196–198 (1992) 415.

[6] N. Yoshida, A. Nagao, K. Tokunaga, K. Tawara, T. Muroga, T. Fujiwara, S. Itoh, and the TRIAM group, Radiat. Eff. Def. Solids 124 (1992) 99.

[7] T. Hirai, K. Tokunaga, T. Fujiwara, N. Yoshida, S. Itoh, the TRIAM group, J. Nucl. Mater. 258–263 (1998) 1060.

[8] S. Itoh et al., in: Plasma Physics and Control Nuclear Fusion Research, Proceedings of the 11th International Conference, Kyoto, IAEA-CN-47/H-II-3, 1986.

[9] T. Hirai, T. Fujiwara, K. Tokunaga, N. Yoshida, S. Itoh, and the TRIAM group, in: Fusion Energy 1998, Proceedings of the 17th Internatinal Conference, Yokohama, 1998, IAEA-CN-69/FT2/3.

[10] D.B. Williams, C.B. Carter, Transmission Electron Microscopy, Plenum, New York, 1996, p.145.

[11] D. Reiter, Trans. Fus. Technol. 29 (1996) 267.

[12] S. Itoh et al., in: Proceedings of the 13th International Conference on Plasma Physics and Nuclear Fusion Research, Washington, D.C. 1990 (IAEA Vienna, 1991) Vol. 1, p. 733.

[13] N. Yoshida, F.E. Fujita, J. Phys. F 2 (1972) 1009.