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Hydrogen release from deposition layers formed from 316 stainless steel by hydrogen plasma sputtering

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ABSTRACT

Deposition layers were formed from type 316 stainless steel by a sputtering method using hydrogen RF plasma at 110 °C, 150 °C and 200 °C. Hydrogen release behavior from the deposition layers was observed by a thermal desorption method and hydrogen retention and release rate were quantified. The values of hydrogen atomic ratio in the deposition layers were in the range from 0.12 to 0.17 as H/(Fe+Cr+Ni+Mo). These values are in agreement with the values of H/W and He/W in tungsten deposition layers. Hydrogen atomic ratio to metal atoms in a metallic deposition layer seems not to depend on the kind of the metal constituting it. It was observed that the microstructure of the deposition layer obviously differed depending on the substrate temperature.

1. Introduction

Understanding of mass transfer between plasma and wall is an important issue from viewpoints of fuel control and radiation safety of tritium. Stainless steels face to plasma as a structural material of diagnostic equipment and a first wall material of fusion experimental devices such as Large Helical Device (LHD). When a stainless steel wall is eroded by sputtering, elements such as Fe, Ni, Cr and Mo are emitted into plasma. These emitted metal atoms form mixed layers and dust in the vessel of a reactor. Actually, dust consisting Fe, Ni and Cr has been observed in the LHD [1]. Many studies about hydrogen retention in carbon deposition layers have been performed [2–4]. However, hydrogen trapping in metallic deposition layers has not been studied sufficiently so far. It has been reported by the present authors that tungsten deposition layers formed from hydrogen isotope plasma trap a large amount of hydrogen isotope [5–7]. It was also found that a tungsten deposition layer that formed from helium plasma contains a large amount of helium [7]. In the present study, deposition layers were formed from type 316 stainless steel by a sputtering method using hydrogen RF plasma and hydrogen release behavior was investigated by a thermal desorption method.

2. Experimental

Deposition layers were formed by utilizing a capacitively-coupled hydrogen RF plasma. An RF plasma device [7] and the experimental procedure [5] have been mentioned in previous papers. The base pressure of the RF plasma device is about 10^{-2} Pa. A stainless steel plate (type 316, 50 mm × 50 mm, 1 mm in thickness, Nilaco Co.) was fixed as a target on the electrode where an RF power is supplied. Formations of the deposition layer were carried out at three different temperatures. Experimental conditions are summarized in Table 1. The deposition layers were formed on tungsten substrates. The influence of the substrate temperature on plasma parameters such as electron density was previously investigated by a Langmuire probe method. The weight of the deposition layer was derived from the weight change of the substrate before and after plasma discharge.

In order to observe hydrogen release behavior from the deposition layer, thermal desorption experiment was conducted. The deposition layer with substrate was packed into a quartz reaction tube. The reaction tube was filled with argon gas and heated from 200 °C to 1000 °C in 100 °C step every 3 h by an electric furnace. Argon gas was introduced into the reaction tube every 30 min in order to transport the desorbed hydrogen into a gas chromatograph. It was previously confirmed that hydrogen release from the deposition layer is negligible below 200 °C.

Surface observation of the deposition layer was performed by a scanning electron microscopy (SEM:SS-550, SHIMAZU Co.). Atomic ratio (at%) on the deposition layer was obtained by an energy dispersive X-ray (EDX:Genesis2000, EDAX Inc.) equipment. The SEM and EDX used in this study were installed at the Center of Advanced Instrumental Analysis, Kyushu University. Microstructures of the deposition layers were observed by transmission electron microscopy (TEM:JEM-2000EXII, JEOL Ltd.) which was installed at the Research Institute for Applied Mechanics, Kyushu University.

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Table 1
Experimental conditions.

Gas	H_2		
RF power [W]	100		
Substrate temperature [°C]	110	150	200
Gas pressure [Pa]	10		
Gas flow rate [cm^3/min]	1.2		
Electrode distance [cm]	8		
Discharge period [h]	240		

3. Results and discussion

3.1. Plasma parameters and elemental analysis

Ion flux slightly increased with an increase of the substrate temperature. But other parameters did not depend on the substrate temperature. Electron density and electron energy were quantified to be $1.1 \times 10^{16}\ m^{-3}$ and 2.0 eV, respectively. Plasma space potential was quantified to be 30 V. An averaged value of ion flux in the range from 114 °C to 300 °C was obtained to be $1.2 \times 10^{20}\ m^{-2}s^{-1}$. Atomic ratios in the deposition layers formed at three different temperatures are summarized in Table 2. Values in parentheses are the ratios of metal atoms in the deposition layers. For comparison, the ratio of metal atoms in 316 stainless steel is also indicated in this table. More than 30% of oxygen was observed in the deposition layers formed at 150 °C and 200 °C. It is considered that a part of metal element was oxidized with the oxygen that originates in a small amount of water vapor that remains in the plasma chamber.

3.2. Hydrogen release behavior

Every time temperature was raised, hydrogen desorption quickly started but then slowly continued. The amount of hydrogen released at each temperature was different in each sample. For instance, a large peak at 700 °C was observed from only the deposition layer formed at 110 °C. From these release behavior, the deposition layer seems to have a releasable amount at each temperature. Furthermore, this amount is different depending on the substrate temperature when the layer was formed. This means that a certain amount of hydrogen is left in the deposition layer at a given temperature. Here, it is assumed that the release rate of hydrogen is proportional to a square of the amount of releasable hydrogen. When the amount of hydrogen left at a temperature of T [K] is expressed as hydrogen retention $q_{R,T}$ [mol/g], the release rate is represented as follows:

$$\frac{dq}{dt} = -k(q - q_{R,T})^2 \quad (\text{mol/g} \cdot \text{s}), \tag{1}$$

where q is the amount of hydrogen in the deposition layer [mol/g], t is time [s] and k is the recombination coefficient [g/mol·s]. The curve fitting was carried out against experimental release curves using Eq. (1). k and $q_{R,T}$ were used as parameters. Hydrogen release at 900 °C or more could be ignored because the amount of released hydrogen was in the same levels as the background. The comparison of the fitting curves and the experimental curves is shown in Fig. 1. The fitting curves agreed very closely with experimental ones. When it was assumed that the hydrogen release rate is proportional to first-order of the amount of releasable hydrogen, the fitting curve was not in agreement well with the experimental curve. Therefore, it can be said that the rate determining step in the hydrogen desorption process is a recombination reaction of hydrogen atoms. The temperature dependence of hydrogen retention is shown in Fig. 2. As shown in this figure, a high temperature above 700 °C is needed to remove the hydrogen trapped in the deposition layer. The values of hydrogen retention in two deposition layers formed at 150 °C are a little different. A slight difference of local conditions such as ion flux and deposition rate at the positions where the substrates were mounted might influence hydrogen retention. Fig. 3 shows the recombination coefficient, k obtained for each deposition layer. As shown in this figure, the value of k decreases gradually with increasing temperature. Especially, k for 110 °C and 150 °C decreases linearly between 200–600 °C and

Table 2
Atomic ratios in deposition layers.

Element	Substrate temperature [°C]			SUS316
	110	150	200	
Fe	70.0	43.0 (68.6)	49.1 (71.1)	65–72
Cr	18.0	11.6 (18.5)	10.5 (15.1)	16–18
Ni	10.8	7.1 (11.3)	8.9 (12.8)	10–14
Mo	1.2	1.0 (1.6)	0.7(1.0)	2–3
O	0.0	37.3	30.9	-

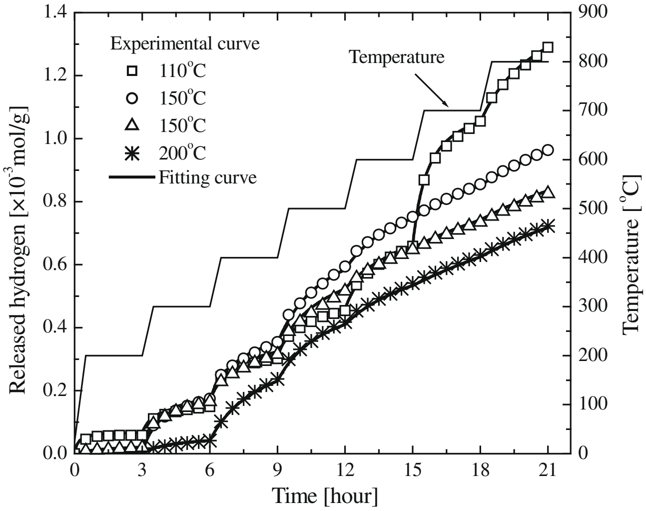

Fig. 1. The comparison of the fitting curves with the experimental ones.

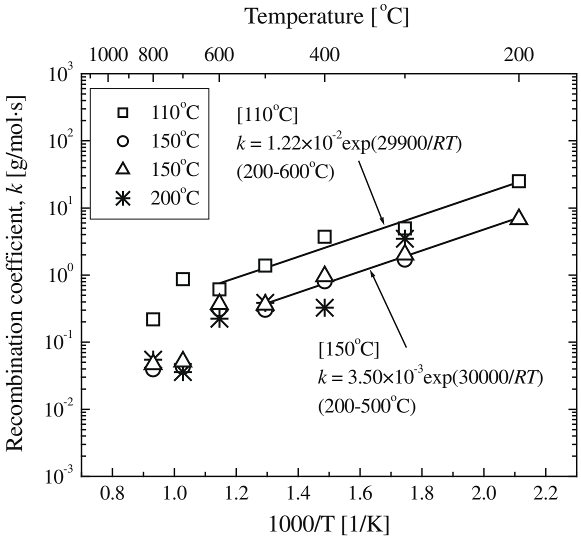

Fig. 2. Temperature dependence of hydrogen retention in deposition layers formed from 316 stainless steel.

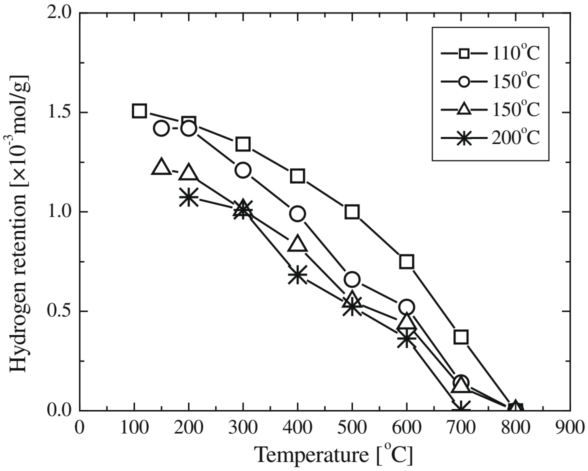

Fig. 3. Recombination coefficient of hydrogen on deposition layers formed from 316 stainless steel.

200–500 °C, respectively. The following values were obtained by a least squares method:

$$k_{110} = 1.22 \times 10^{-2} \exp(29900/RT) \quad (\mathrm{g/mol \cdot s})[200\text{–}600^{\circ}C], \tag{2}$$

$$k_{150} = 3.50 \times 10^{-3} \exp(30000/RT) \quad (\mathrm{g/mol \cdot s})[200\text{–}500^{\circ}C], \tag{3}$$

where R is the gas constant [J/mol·K]. k for 200 °C is comparable with k for 150 °C though the linearity is not observed. In general, it is said that the recombination coefficient greatly depends on the surface condition such as the amount of impurities and microstructure. The surface condition of the deposition layer might change as temperature was raised. Surface observation and elemental analysis of the deposition layer was performed before and after heating. Initially the surface of the deposition layer was smooth but it became lumpy by heating. It was also found that the atomic ratio of oxygen in the layer increased to 60%. The oxidation of a deposition layer is considered to be promoted by heating. Because these changes and hydrogen desorption take place at the same time, the value of k is considered to scatter at comparatively high temperature.

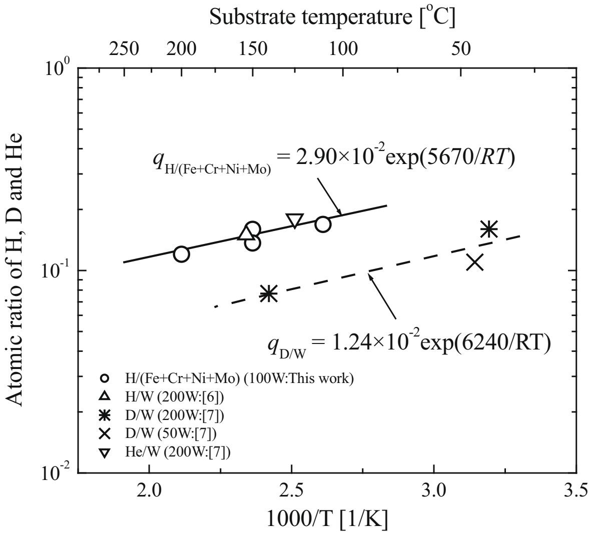

Fig. 4. The comparison of H/(Fe+Cr+Ni+Mo) in deposition layers formed from 316 stainless steel with H/W, D/W and He/W in tungsten deposition layers.

3.3. Atomic ratio in deposition layers

The atomic ratio represented as H/(Fe+Cr+Ni+Mo) was estimated from the weight of deposition, the ratio of metal atoms, and total amount of released hydrogen. The estimated values are shown in Fig. 4. For comparison, the values of H/W, D/W and He/W in tungsten deposition layers previously obtained are also shown in this figure [7]. Hydrogen atomic ratio in the deposition layers formed from stainless steel is in agreement with the values of H/W and He/W in tungsten deposition layers. Hydrogen atomic ratio to metal atoms in a metallic deposition layer seems not to depend on the kind of the metal constituting it. On the other hand, deuterium atomic ratio in a tungsten deposition layer is smaller than hydrogen atomic ratio in deposition layers formed from stainless steel and tungsten. The value of retention may have isotope effect. The values of H/(Fe+Cr+Ni+Mo) of the deposition layer formed from 316 stainless steel and the value of D/W of the deposition layer formed from tungsten were obtained respectively by a least squares method as follows:

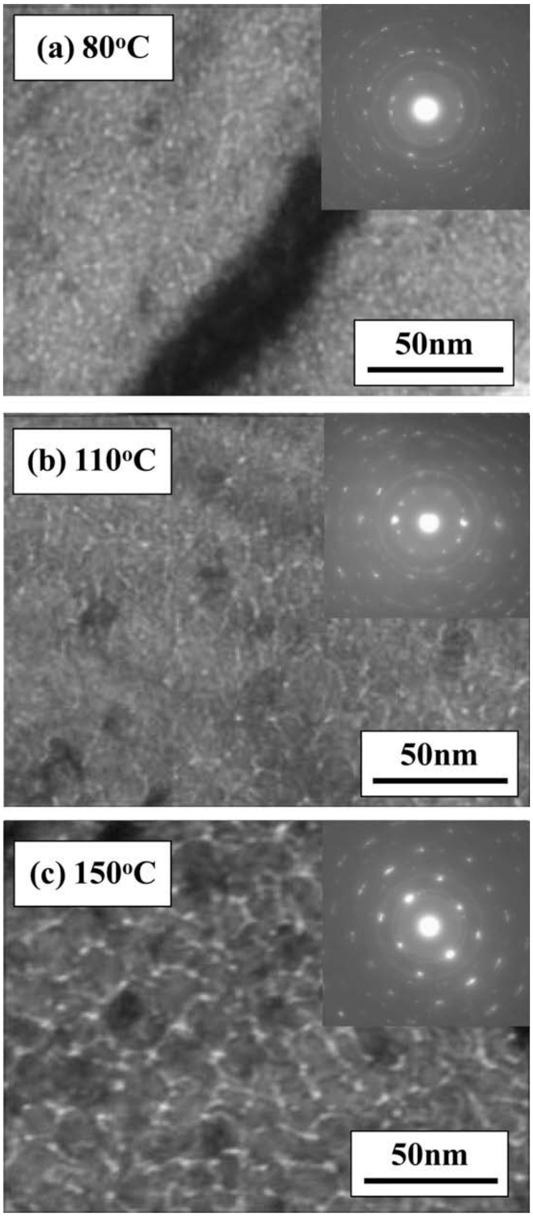

Fig. 5. TEM images of deposition layers formed from 316 stainless steel.

$$q_{H/(Fe+Cr+Ni+Mo)} = 2.90 \times 10^{-2} \exp(5670/RT)[110-200^{\circ}C] \quad (4)$$

$$q_{D/W} = 1.24 \times 10^{-2} \exp(6240/RT)[40-140^{\circ}C] \quad (5)$$

where R is the gas constant [J/mol·K].

3.4. Observation of microstructure

Fig. 5 shows TEM images (bright field) of the deposition layers formed at 80 °C, 110 °C and 150 °C by 2.5-hour plasma discharge. White dots in the image of (a) indicate bubbles. The deposition layer formed at 80 °C has a numerous bubbles of a few nanometers. On the other hand, white contrast in the images of (b) and (c) shows the grain boundary. The electron diffraction patterns indicate light spots and rings from deposition in addition to strong spots from substrate. These results indicate that grains grow up gradually as the substrate temperature becomes high. It can be said that the microstructure obviously differs depending on a slight difference of substrate temperature. It is speculated that hydrogen is trapped in a part of disordered structure such as bubbles and grain boundaries. As the substrate temperature becomes higher, defects and grain boundaries reduce gradually. As a consequence, hydrogen retention in the deposition layer is considered to decrease depending on the substrate temperature.

4. Conclusions

Deposition layers were formed from 316 stainless steel by hydrogen plasma sputtering at three different temperatures. Hydrogen release behavior from the deposition layer was observed and hydrogen retention and release rate were quantified. Hydrogen atomic ratio as H/(Fe+Cr+Ni+Mo) in deposition layers formed from stainless steel is in agreement with H/W and He/W in tungsten deposition layers. Hydrogen atomic ratio to metal atoms in a metallic deposition layer seems not to depend on the kind of the metal constituting it. The microstructure of the deposition layer obviously differed depending on a slight difference of the substrate temperature. For this reason, hydrogen retention is considered to be different depending on the substrate temperature.

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References

[1] J.P. Sharpe, V. Rohde, The ASDEX-Upgrage Experiment Team, A. Sagara, H. Suzuki, et al., J. Nucl. Mater 313–316 (2003) 455.
[2] J.P. cord, N. Bekris, J.D. Elder, S.K. Erents, D.E. Hole, K.D. Lawson, G.F. Matthews, R.-D. Penzhorn, P.C. Stangeby, J. Nucl. Mater. 290–293 (2001) 224.
[3] C.H. Skinner, C.A. Gentile, G. Ascione, A. Carpe, R.A. Causey, T. Hayashi, J. Hogan, S. Langish, M. Nishi, W.M. Shu, W.R. Wampler, K.M. Young, J. Nucl. Mater. 290–293 (2001) 486.
[4] K. Katayama, H. Nagase, Y. Manabe, Y. Kodama, T. Takeishi, M. Nishikawa, Thin Solid Films 457 (2004) 151.
[5] T. Kawasaki, Y. Manabe, K. Katayama, T. Takeishi, M. Nishikawa, Fusion Sci. Tech. 48 (2005) 581.
[6] K. Katayama, K. Imaoka, T. Okamura, M. Nishikawa, Fusion Eng. Des. 82 (2007) 1645.
[7] K. Katayama, K. Imaoka, T. Tokitani, M. Miyamoto, M. Nishikawa, S. Fukada, N. Yoshida, Fusion Sci. Tech. 54 (2008) 549.