Growth of multifractal tungsten nanostructure by He bubble induced directional swelling

Shin Kajita¹, Naoaki Yoshida¹, Noriyasu Ohno¹ and Yoshiyuki Tsuji³
¹ EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan
² Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
³ Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
E-mail: kajita.shin@nagoya-u.jp

Key words: nanostructure, plasma, helium bubbles

Abstract

Helium (He) plasma irradiation to tungsten (W) leads to morphology changes in nanometer scale by the formation and growth of He bubbles. Initially pinholes and protrusions are formed on the surface followed by the formation of nanostructures. In this study, based on experimental observation, the growth process of the fiberform nanostructures are revisited and the swelling process of the structure is discussed. The novel nanostructures are analyzed from the viewpoint of fractality. It is found that the number of the initially formed pinholes and its sizes have a fractal relation, indicating that the size and number of bubbles formed near the surface have fractality. The fractal dimension is estimated from the brightness variation of a transmission electron microscope (TEM) micrograph and gas adsorption property. Moreover, it is revealed from TEM image analysis that the nanostructure has multifractal feature, probably because of the fractality identified between the number and the size of bubbles near the surface.

1. Introduction

It has been revealed in the mid-2000s that fiberform nanostructures are grown on tungsten (W) surfaces by the exposure to helium (He) plasmas [1]. The formation of the nanostructure has been initially identified in basic plasma material interaction study in nuclear fusion devices. The nanostructures have pros and cons for plasma facing materials in nuclear fusion devices. On the one hand, it can suppress particle emission from the surface [2] and formation of cracking [3]. On the other hand, the nanostructure is so fragile to transient heat loads that it can increase the amount of W erosion in response to transient pulsed heat load accompanied by so called edge localized modes [4]. In addition to fusion researches, attention has been paid from the viewpoint of its potential application. It can be used for solar absorber for solar thermophotovoltaic system by taking advantage of its high optical absorptivity [5]. It has been identified that it has a significant photocatalytic activities for decomposing organic materials [6, 7] and water splitting [8]. Also, the reduction in the laser ablation power threshold may have an advantage for industrial application [9], and it can be used for electron emitter by making use of the fact that the field emission current is significantly increased by the nanostructurization [10]. By considering the fact that the formation of nanostructures by the He plasma irradiation were identified on various other metals such as molybdenum [11, 12], iron [6, 13], titanium [14], and nickel [6], possible application fields can expand further. Moreover, recent studies demonstrated that nanostructured W can be fabricated using magnetron sputtering devices [15, 16], suggesting the sufficient potential to be used for industrial application.

The growth of nanostructures involves novel processes and has been investigated from experimental and theoretical point of view. Experimentally, from the fact that the growth rate of the thickness of the nanostructured layer is in proportional to the square root of the He fluence, it was suggested that a diffusion process was related to the growth mechanism [17]. Detailed transmission electron microscope (TEM) observation revealed that the growth of He bubbles is deeply related with the growth of the nanostructures [18]. From theoretical point of view, a viscoelastic model tried to explain the nanostructure growth rate and
formation temperature range [19], and adatoms diffusion model supported the existence of the threshold in the incident ion energy and also the growth rate of the layer thickness [20]. Moreover, extensive simulation studies have been conducted. It can be said that there are two target issues to be attacked by simulation: one is the formation of He bubbles and the other is the formation of nanostructures with the growth of He bubbles. Molecular dynamic (MD) [21, 22] and first-principles simulation [23] indicated that He atoms in W are attracted each other and form He clusters. Numerical analysis of dynamic He cluster behavior also indicated that bubbles within a tendril are grown by self-trapping effects of He [24]. Bursting of He bubbles [25] and the formation of foams and fuzz structures [26] are demonstrated using a hybrid MD and Monte Carlo simulation. To fully understand the physics behind the nanostructure growth, it is of importance to further advance the theoretical and numerical studies and to compare the results with experimental observations.

This study will revisit the growth process of the nanostructures based on experimental surface analysis and add a potential mechanism of material swelling. Moreover, fractal feature of the He irradiated W will be revealed. Concerning the fractality of the nanostructure, the fractal dimension and the fractality in the material density versus height have been revealed recently [27]. In this study, in addition to the fractal dimension and the scale ranges where fractal relation can be identified, we anatomize the fractal features of the nanostructures from following two different aspects: one is the initially formed pinholes on the surface and the other is a multifractal analysis from a TEM micrograph. Although it may not be easy to discuss the growth mechanism of nanostructures directly from the fractal analyses, quantification of the nanostructures will be important to check the validity of models when comparing simulation and theoretical results and experimental observation.

2. Revisit the growth process

2.1. Preparations

Experimental observation and analysis of W samples exposed to He plasmas are the basis of this study. Here, we briefly describe the setup and basics of the experiments. The irradiations were conducted in the linear plasma device NAGDIS-II [28], which has been used to investigate phenomena that occurs in the divertor regions in nuclear fusion devices. In the NAGDIS-II device, the plasma is produced in steady state by a direct current arc discharge using an LaB₆ cathode. The typical electron density and temperature of the He plasma are $\sim 10^{19}$ m$^{-3}$ and $\sim 5$ eV, respectively. The plasma produced in the source region is diffused to the downstream region along with the magnetic field line. The samples are installed in the downstream region, which is $\sim 1.5$ m far from the plasma source. The incident ion energy is controlled by changing the biasing of the sample, and the surface temperature is mainly controlled by changing the plasma density. The sample temperature is measured by a radiation pyrometer. After the plasma exposure, the samples were analyzed by scanning electron microscope (SEM) and TEM, and gas absorption was measured using krypton (Kr) gas by changing the relative pressure.

2.2. Observation

Figure 1 shows the He plasma irradiated surface observed by SEM and TEM. The He irradiation was conducted at the incident ion energy of 50 eV and the surface temperature of 1400 K, and the exposed He fluence was $0.6 \times 10^{23}$ m$^{-2}$. The He ion flux was $1.6 \times 10^{22}$ m$^{-2}$, and the irradiation time was 375 s. It is noted that the He fluence of $2-3 \times 10^{22}$ m$^{-2}$ is necessary to fully develop the nanostructures on the surface, and this case represents the initial feature of the nanostructure growth. Figure 1(a) is an SEM micrograph observed from top with a cross sectional micrograph in the inset. Formation of pinholes and protrusions are identified on the surface. Protrusions with the height of 100–200 nm were observed in the cross-sectional micrograph. It is likely that the rough structures shown in a white circle corresponds to the protrusions similar to the ones identified in the cross-sectional image.

Figures 1(b)–(f) are cross-sectional TEM micrographs of the sample, which was fabricated with a focused ion beam milling. The thickness of the sample was $\sim 300$ nm in figures 1(b) and (c), while it was $\sim 50$ nm in figures 1(d)–(f). Top of the TEM samples was covered by carbon to sustain the structure during and after the milling process. In figures 1(b) and (c), ring structures and protrusions with the height of <200 nm are observed on the surface. The width of the protrusion with the height of $\sim 200$ nm seen in figure 1(c) is typically 50–80 nm. Because the thickness of the sample is greater than the size of the holes, the holes here represent rings rather than bubbles embedded on the structure. Also because the surface was coated by carbon before the milling process, the structures were fixed during the TEM sample preparation. Since the background carbon contrast did not change, it can be said that the cave structures should be original structure and not be formed during the milling process. The observation of ring structures was reported in [29], in which the initial growth process was revealed by utilizing the fluence dependence appeared on the boundary between the irradiated and non-irradiated parts. The outer diameter of the ring observed in [29] was in the range of 70–150 nm, which was comparable to those observed in figures 1(b) and (c).
Figure 1(d) shows the cross-sectional TEM image of a thin sample in a low magnification. It is found that there is a rough layer with bubbles on the surface with the thickness of $\sim 200$ nm. Figures 1(e) and (f) are enlarged micrographs of the sample. In the growth process, blisters such as seen in figure 1(e) are formed first and finer protrusions probably formed by the bursting of blisters, as seen in figure 1(f), are likely to play an important role to the growth of the nanostructures.

Figure 2 show SEM and TEM micrographs of the sample with approximately twice higher He fluence of $1.1 \times 10^{25}$ m$^{-2}$. The irradiation was conducted at the same surface temperature and the incident ion energy to those in figure 1. Figure 2(a) is an SEM micrograph observed from top with a cross sectional SEM in inset. Roughness is enhanced compared with figure 1, and protrusions became finer and longer. The extended fine structure from the surface can be clearly seen in figures 2(b)–(d), which were observed from oblique direction. It is seen that the whisker like structures, typically with the length of up to 500 nm, are grown from some locations. It is interesting to note that the whisker like structures are grown individually without forming network like structures. Recently, it was observed from experiments in a linear device that longer whisker like structure, typically $>1 \mu$m, has been extended from the surface [30]. Although the mechanism of the non-uniform growth has not been fully understood yet, the result indicates that there is a growth process of structure in the length direction. In figure 2(d), loop structures are also identified; the size of the loop is greater than those in figure 1 and the shape is not circular. It is more likely that two fibers are connected and formed a loop than they were grown from the same place. It is thought that fusion bonding occurs and connects the two fibers easily when they are attached each other during the plasma irradiation. In figure 2(d), where a part of the cross section is also seen, bubbles are also identified at (close to) the surface.

Figures 2(e) and (f) shows TEM micrographs with the sample thickness of $\sim 300$ nm. The number of protrusions with the height of 100–200 nm increased from figure 1. In some locations, parts of finer and longer structures are seen. Inner structure can be clearly identified when the sample thickness is $\sim 50$ nm, as shown in figures 2(g)–(i). The surface becomes very rough in the scale of the order of $\sim 100$ nm, and the structure contains massive amount of He bubbles inside. A pair of a protrusion and a hole seen in the central part of figure 2(i) was likely to be formed by the bursting process of the skin of a blister.
Figures 3(a)–(c) shows TEM micrographs of He irradiated W. The irradiation was conducted at the surface temperature of 1400 K, and the He fluence was $5.4 \times 10^{25} \text{ m}^{-2}$. It is observed that each structure has bubbles inside. It is seen from figure 3 that the structures are not straight. Some curved structures would be intrinsic, but some part might have been twisted in the observation process. A part of the structures were peeled off from the sample, placed on a mesh, and observed by TEM. It is noted that structures are not only extended in the length direction but also more than three different directions in some parts and forms network like structure. It is unlikely that the more than two fiberform structures were grown from one protrusion or a node of structure. Rather, two fiberform structures fused together when they were attached during the irradiation process where the structure temperature was $\sim 1400$ K. Even below the melting point, sintering can occur as annealing significantly deformed nanostructures when the surface temperature was higher than $\sim 1000$ K [31]. In addition, an interesting point we can identify in figure 3 is the fact that the structure has narrow part in places, as indicated with red arrows. Dotted circles present the position where the structure was likely to be broken at such narrow part, indicating that the narrow part is weak in the structure. We speculated that the narrow part was formed by the bursting of bubbles from the side of the fiber.

Figure 4 shows the distribution of the structure width (diameter). Some isolated parts are extracted from figures 3(a)–(c), and the width was measured. There are peaks around 20–30 nm and tails from 5 to 45 nm. Although there are three peaks, they may disappear if more samples are used to get the profile. The distribution could be altered when the irradiation temperature changed. The width becomes wider as increasing the surface temperature, as shown in [11]. It is thought that this non-uniformity is related with the growth mechanism. From figure 4, it is seen that typical structure width is 20–30 nm. The narrow parts has $\sim 10$ nm or less and there are nodes with wider width than 30 nm which may be connected to other structure three-dimensionally.

2.3. One-dimensional swelling process

Figure 5 shows schematics of the proposed growth process of the nanostructures during He plasma irradiation. Figures 5(a)–(c) describe three different processes to discuss each process individually, though the processes would occur all together. Figure 5(a) shows an implantation process: He particles are implanted from the surface, and nano-bubbles formed near the surface diffuse to inside. The implanted He atoms diffuse and migrate three-dimensionally, and coalescence of He atoms leads to formation of He nano-bubbles, as shown in figure 5(b).

Volumetric swelling of material would occur by the formation of He clusters and nano-bubbles. A fraction of nanobubbles disappeared on the surface of the structure, and, consequently, swelling in radial direction of fiberform nanostructure is resolved. On the other hand, swelling in the axial direction would remain, because inflow and outflow of bubbles are balanced on the boundary. Large sized bubbles, which do not move, absorb nano-bubbles and grow further. Figures 6(a)–(e) shows schematics of the growth process of the nanostructures during the He plasma irradiation.

On the surface of He irradiated W samples, plate like structures have been identified by TEM observation in the nanostructure forest [18]. It is likely that the similar swelling process could occur on plate in two-dimensionally. The area of the plate could be expanded while decreasing the thickness. Recently, a growth of
Figure 3. TEM micrographs of the He irradiated nanostructures. The irradiated He fluence was $5.4 \times 10^{25} \text{ m}^{-2}$. Red arrows show narrow part of fibers, and, in circles, the structures were likely to be broken at narrow parts.

Figure 4. Nanostructure widths as measured from the TEM images in figure 3.
distinct nano-wall were observed on platinum plate by the exposure to He plasma [32]. It would be possible that structure is expanded two-dimensionally in a similar growth process. In addition to the processes in figure 5, there would be another mechanism to thin down the structure. One possibility is the process that the structure width decreases little by little when bubbles reach the surface consecutively. If the narrowing occurs more effectively than the swelling in the radial direction, then the axial swelling can occur together with the narrowing process. The proposed mechanism does not necessarily deny the processes of material flow to the nanostructures proposed in [19]. However, it may be possible that directional swelling process can explain the extension of the structure at least in the initial formation process. For example, from figures 1 to 2, the typical structural width decreased from 50–80 to 30–50 nm and the height increased from ~200 to 500 nm. The decrease in the width by a factor of 1.6 indicated the possibility of the axial extension by a factor of ~2.5 without significant volumetric swelling.

Figure 5. Schematics of the swelling process of W during the He plasma irradiation. (a)–(c) show implantation process, diffusion process, and swelling process, respectively.

Figure 6. Schematics of the growth process of the nanostructures during the He plasma irradiation. The He ion fluence increases from (a) to (e). Typically all the processes occurs when the He ion fluence is less than $10^{25}$ m$^{-2}$.
3. Fractal analysis

3.1. Pinholes

The formation of pinholes on the surface can be identified during the He plasma irradiation when the He fluence is less than $10^{25}$ m$^{-2}$ or the incident ion energy was less than approximately 20–30 eV. The formation of rather large pinholes have been identified on the annealing process of He irradiated samples [33].

Here, let us focus on the pinholes on the surface, which can be presented as black holes on the SEM micrographs. Because SEM sees secondary electron emission from the surface, pinholes are presented as lower brightness area. Figure 7(a) shows SEM micrographs of the He irradiated surfaces with various He fluences, i.e., from the left, 0.6, 1.8, and $4.7 \times 10^{25}$ m$^{-2}$. The incident ion energy and the surface temperature were 55 eV and 1800 K, respectively. With increasing the He fluence, the roughness is enhanced and the fiberform nanostructures are seen when the He fluence was $4.7 \times 10^{25}$ m$^{-2}$. Figure 7(b) shows digitized images of the ones in figure 7(a) with using a threshold with which only holes are identified. Figure 7(c) shows the number density of holes as a function of the hole area measured from digitized images. In the double logarithmic plot, the relation between the number of the holes, $N_h$, and the hole area, $S$, can be well on a line, up to the hole area of $\sim 10^4$ nm$^2$. In other words, following power distribution is satisfied when $S < 10^4$ nm$^2$:

$$N \propto S^{-D/2}. \quad (1)$$

The factor of two was used in equation (1) to discuss later the relation between the number and the characteristic length of holes, i.e. diameter if the hole is circular. The size $S \sim 10^4$ nm$^2$ corresponds to a square with the length of 100 nm, meaning that the power law was satisfied when the size of the hole is typically $\sim 100$ nm in diameter assuming that the shape of the holes are circle. From the cross sectional TEM micrographs shown in figure 1 and [18], it is seen that the thickness of the bubble formed layer below the rough structure is approximately 100 nm. It is likely to be difficult to form bubbles with larger sizes compared with the thickness of the layer. Bubbles are

![Figure 7](image-url)
likely to be burst rather than growing. The value \( D \) corresponds to the steepness of the slope, and it increases with the He fluence: \( D = 0.95, 1.70, \) and \( 2.40 \) at the He fluence of \( 0.6, 1.8, \) and \( 4.7 \times 10^{25} \) \( \text{m}^{-2} \), respectively.

Typical example exemplifies the fractal relation between the size and the number is in the crater on the moon \([34, 35]\). The number of the crater on the moon, \( N_c \), has the power law relation with the diameter of the crater on the moon, \( d \), as \( N \propto d^{2.0} \). It is interesting to note that \( D \) would be two when the He fluence was \( \sim 3 \times 10^{25} \) \( \text{m}^{-2} \) in the case of pinholes on W. It was discussed that the size of the crater was determined by the size of the meteorites hit on the moon. In the present situation, the size of pinholes is determined by the size of the He bubbles existing near the surface. Thus, figure 7(c) indicates that the number and the size of He bubbles have fractal relation. In other words, the number of the He bubbles increases with decreasing the size in accordance with the power law. For the case of He bubbles, the slope is probably determined not only by the He fluence but also other parameters such as the surface temperature. Detailed investigation for the other parameter dependences remains ongoing.

3.2. TEM analysis

Figure 8(a) shows a TEM micrograph of the W nanostructure. The sample is vacuum plasma spray W and the He plasma irradiation was conducted at the surface temperature of 1600 K with the ion energy of \( \sim 10 \) eV up to the He fluence of \( 4 \times 10^{27} \) \( \text{m}^{-2} \). It is noted that the nanostructures have been formed by the irradiation at the energy of \( <20\sim 30 \) eV only on vacuum plasma spray tungsten. Porous structure can be clearly seen inside the structure. The contrast of the TEM image reflects mass-thickness and Bragg contrast. To focus on the mass-thickness contrast, significantly darkened areas where Bragg’s law was satisfied were not used for the analysis. In this study, the brightness of an image is used for the fractal analysis. The brightness levels of total black and white correspond to 0 and 255, respectively. The variation of the brightness level is calculated as

\[
\Delta b(l) = \left\langle \left[ b(x, y) - b(x_0, y_0) \right]^2 \right\rangle^{1/2},
\]

where \( l \) is the distance between the positions \( (x, y) \) and \( (x_0, y_0) \), and the brackets \( \langle \rangle \) means the average. The position \( (x_0, y_0) \) is fixed and the position \( (x, y) \) is changed while taking the average. To use the value of
brightness, it should be confirmed that \( b \) is proportional to the corresponding physical value, i.e., here, mass-density. Since the brightness is decreased by the electron scattering in mass-thickness contrast, it decreases exponentially along with the beam line. However, the brightness can be basically expressed with a linear relation as the first order of the exponential function, because the samples used in the present study is so thin that transmission is high.

Then, following relation is satisfied [36]:

\[
\Delta b(l) = l^H.
\]  

(3)

Here \( H \) is Hurst exponents, and the fractal dimension, \( D \), can be obtained from the relation \( H = 3 - D \). This study applied this method to a TEM image. The analysis deduces fractality in the accumulated mass thickness contour of the structure.

Figure 8(b) shows the variation of the brightness level as a function of the distance. The slope of the distribution alters at \( \sim 4-5 \text{ nm} \), which corresponds to the typical size of bubbles existing inside the structure, and power law was satisfied above the knee of the slope. From the slope, the fractal dimension is obtained to be \( 2.65 \pm 0.02 \). Although it is generally difficult to discuss physical meaning from the fractal dimension, typical examples are the Sierpinski gasket and carpet. In two-dimensional cases, the Sierpinski gasket and carpet have the fractal dimension of 1.58 and 1.89, respectively. These structures can be expanded to three-dimensional case easily, and the fractal dimension becomes +1 to that of the two-dimensional case. If we analyze the three-dimensional Sierpinski gasket and carpet in the same manner as in figure 8, the fractal dimensions would be close to 2.58 and 2.89, respectively. It is difficult to directly compare the structural shapes; the fractal dimension expresses the complexity of the structure. It can be said that the fact that figure 8(b) deduced the fractal dimension of 2.65 indicates that the structure is complex shapes with various size of He bubbles inside, as similar to the fact that the Sierpinski gasket and carpet have various size of blank triangles or squares. Moreover, this value itself will have a meaning when comparing with simulation in future.

Note that this fractal dimension reflects not only the surface roughness but also the inner porous structure. Previously, the fractal dimensions estimated from the cross sectional SEM micrograph of a fully grown nanostructured W was typically \( 2.38 \pm 0.2 \) in the scale less than \( 10-20 \text{ nm} \) and \( 2.85 \pm 0.03 \) in the larger scale [27]. The obtained value of \( 2.65 \pm 0.02 \) was in between the two values obtained. Although the irradiated temperature in [27] was 100 K less than that for the present study, it is likely that they have similar structure. Assuming that the structures are similar, the difference in the scale and fractal dimension between SEM and TEM could indicate the influence of the inside bubbles on the surfaces. In other words, the surface roughness is likely to be characterized principally by the inner porous structure, but the influence may alter when bubbles arrive on the surface. Also, there is a possibility that SEM may also contain the information of inner porous structure, because the portion of electrons is penetrated to some extent of the order of nanometers. For future work, a comparative investigation between SEM and TEM analysis using the same sample is of importance for further discussion.

### 3.3. Multifractality

Let us generalized the fractal property by analyzing the TEM image from the view point of multifractality. First, count the sum of brightness of all the pixels in a circle from a reference point with the radius \( r \) as

\[
B(r) = \sum_i b_i(r).
\]

(4)

Here, \( b_i(r) \) is the brightness of \( i \)th pixel in the circle, and define \( p_i(r) \) as

\[
p_i(r) = \frac{b_i(r)}{B(r)}
\]

(5)

Generalized fractal dimension is defined as [34, 35]

\[
D_q = \lim_{r \to 0} \frac{1}{q-1} \ln \chi(q) = \ln r,
\]

(6)

where

\[
\chi(q) = \sum_i p_i(r)^q.
\]

(7)

The value \( q \) is the moment of order [35]. Choosing large value of \( q \) favors contributions from cells with relatively high values of \( p_i \) since \( p_i^q \gg p_j^q \), with \( p_i > p_j \), while \( q < -1 \) favors the cells with relatively low values of the measure \( p_i \). That is, when \( q \) is sufficiently negative, the influence of pixels with low brightness is enhanced, while the influence of pixels with high brightness is enhanced when \( q \) is positive. For \( q = 0 \), the fractal dimension \( D_0 \) corresponds to normal box-counting dimension. In other words, when \( q = 0 \), which corresponds to mono-
In analysis case, the variation of contrast of image was not taken into consideration. As changing the moment order \( q \), the influence of brighter or darker contrast parts are emphasized for the analysis. Practically, the right hand side of equation (6) is obtained from the slope of the double logarithmic plot of \( \chi(q) \) against \( r \).

To apply this method to the TEM micrograph, it was first necessary to inverse the contrast and subtract the background brightness, as shown in the inset of figure 9(a). Moreover, it was necessary to decrease the resolution of brightness to eliminate artificial error especially when \( q \ll 0 \). The resolution from 0–255 was reduced to 0–5. Approximately five reference points are chosen from the circles shown in the inset of figure 9(a), and averaged values are used to obtain the slope to deduce \( D_q \).

Figure 9(a) shows the plot of \( \chi(r) \) as a function of \( r \) for \( q = 0 \). From the slope, fractal dimension was estimated to be \( D_0 = 2.0 \). When \( q = 0 \), regardless of the brightness, the number of pixel is counted if \( b_i(r) > 0 \). In other words, in the scale less than \( \sim 20–30 \) nm, it is likely that \( W \) exists in almost all the cells (pixels) in the circle. The power law relation between \( \chi \) and \( r \) was identified even when \( q \) is altered from \( -5 \) to \( 10 \) and \( D_q \) can be obtained as changing \( q \). Figure 9(b) shows \( D_q \) as a function of \( q \). In \( D_q \) versus \( q \) relation, in general, \( D_q \) decreases as increasing \( q \) around \( q \sim 0 \) for multifractal patterns, while the \( D_q \) has almost flat profile for non-fractal and monofractal images. In figure 9(b), from \( q = -5 \) to \( 10 \), \( D_q \) gradually decreased from 2.1 to 1.85. From the fact that \( \chi \) and \( q \) was in power law for various \( q \) and the profile of \( D_q \) was a decreasing function around \( q \sim 0 \), it was identified that the TEM image of nanostructures has a multifractality. When \( q = 0 \) the profile of mass thickness cannot be characterized; multifractal analysis makes it possible to reveal the fact that the spatial profile of mass thickness can be expressed as a sum of fractal sets.

**Figure 9.** In (a), fractal dimension was deduced from the slope of the \( \chi(r) \) versus \( r \) graph. The similar power law relation was satisfied when \( q \) is altered, and the general fractal dimension \( D_q \) deduced from the slope was plotted as a function of \( q \) in (b). (c) is the multifractal spectrum (\( f-\alpha \) relation).
Generalized fractal dimension can be expressed with $\alpha$ and $f(\alpha)$ defined as follows [34, 35]:

$$f(\alpha) = q\alpha - (q - 1)D_0,$$

(8)

$$\alpha = \frac{d}{dq}\left[(q - 1)D_0\right].$$

(9)

Figure 9(c) shows singularity spectrum $f-\alpha$, which is frequently used to illustrate the characteristics of multifractality. In this plot, the spectrum has a peak, and the value corresponds to $D_0$ of 2.0. The corresponding value in $\alpha$ was $\sim 2.0$. Although meaningful analysis can be conducted only in the range of $-5 < q < 10$ due to the limit of the resolution of the image at the moment, it is likely that the spectrum will approach asymptotically to zero when $q$ approached to $+\infty$ and $-\infty$. However, from the present analysis, one can say that the global mass thickness profile of the image can be characterized with a sum of subset with $f(\alpha)$ in the range from one to two.

In general, the spectrum is broader for multifractal patterns compared with monofractal or non-fractal patterns. In other words, as increasing the difference between minimum and maximum $\alpha$ values, the set of the image is expressed as a sum of various subsets with wider fractal dimensions. It is of interests for future work to investigate the difference in singularity spectrum using specimens with different irradiation conditions. Although it is not easy to discuss the physics behind from the singularity spectrum, the spectrum will be also useful for comparing with the simulation results, as was done in other cases [35].

The multifractality of TEM suggests that the pattern has fractal feature when focusing on different contrast levels. When $q << 0$, the generalized fractal dimension is sensitive to low brightness part, while it is sensitive to high brightness part when $q \gg 0$. As was discussed in section 3.1, the sizes of bubbles have variations and likely to have fractal relation with the number. If all the bubbles had same size, the multifractal feature could not appear. It is likely that the variations in the size and the number of bubbles contribute to yield multifractality in the mass thickness profile. In future, before comparing with the sophisticated simulation results, it is of interests to investigate multifractality of the mass thickness contrast of fibers with various types of distributions of bubbles inside and compare with the singularity spectrum in figure 9(c).

3.4. Gas absorption

Fractal feature can also be obtained from gas absorption property. Figure 10(a) is the adsorption isotherms for the He irradiated sample using krypton for the absorption gas. Adsorption isotherm can be obtained by measuring adsorption volume, $V$, while changing the gas pressure $P$. The sample was exposed to the He plasma at the sample temperature and the incident ion energy of 1550 K and 55 eV, respectively. Two different He fluence cases, i.e. $1.3 \times 10^{25}$ and $5 \times 10^{26}$ m$^{-2}$, are shown. Note that since the sample size is different, relative values are only important in figure 10(a).

Although so called multi probe method [37], which uses different gas species, is likely to be more reliable, this study uses a single probe method for simplicity, which infers fractal dimension using a single gas species [38]. Comparative study between the single probe method and multi probe methods suggested that it can deduce reasonable surface fractal dimension [39]. Fractal dimension can be obtained from the following relation:

$$V \propto \left[\ln\left(\frac{P_0}{P}\right)^{D-3}\right],$$

(10)

where $P_0$ is the saturation pressure. The used partial pressure range was $0.05 < P/P_0 < 0.3$, which was limited below the Kelvin condensation step that corresponds to the pore filling [40].

Figure 10(b) shows the He fluence dependence of deduced $D$. Strangely, $D$ decreases with the He fluence from 2.8 to 2.4. At the moment, the reason to explain this behavior has yet to be fully understood; one of the reasons is attributed to the fact that the dealt range here is much smaller than the one in other methods such as TEM and SEM analysis. Applying Kelvin equation, the relation between the radius of the structure and the partial pressure can be roughly estimated as follows for krypton case [41]:

$$r_K = 119.4 \times \left(\frac{P}{P_0}\right)^3 - 60.73 \times \left(\frac{P}{P_0}\right)^2 + 13.25 \times P/P_0 - 0.007.$$ 

(11)

The partial pressure range of $0.05 < P/P_0 < 0.3$ corresponds to $0.5 < r_K < 1.7$ nm. Thus, the deduced fractal dimension does not reflect the complicated nanostructure itself, but it reflects the roughness of the surface of the fiberform structure. Conversely, fractal dimension of 2.4–2.8 in figure 10 indicated that significant roughness in sub-nanometer scale exists on the surface as well. Recently, MD simulation shows the surface roughening occurs by tungsten adatoms on the surface and adatom ‘islands’ [42]; the observed surface roughness in sub-nanometer scale may be associated with adatoms. The decrease of the fractal dimension with the He fluence in figure 10 suggests that roughness in sub-nanometer scale gradually diminishes as the structure becomes finer.
4. Concluding remarks

In this study, the growth process of fiberform nanostructures formed on tungsten (W) surface by the exposure to helium (He) plasmas are revisited. Moreover, fractal features of the He plasma irradiated materials are investigated in four different methods.

From detailed SEM and TEM micrographs, the initial formation process of nanostructures was discussed. It is shown that protrusions were formed and grown during the irradiation. It was likely that protrusions were often originated from the bursting of He blisters.

Width of nanostructure fiber was analyzed using TEM micrographs; it was found that the width of the fiberform structures has a variation from 5 to 45 nm. It was found that there were many narrow parts (typically ∼10 nm); it is thought that the narrow parts are formed in the process that rather large bubbles arrives on the surface and packed He gas is released. We proposed a one-dimensional directional swelling process for the structure growth during the He plasma irradiation. This model is based on the fact that desorption does not occur in the axial direction of the fiber, although absorption and desorption of He particles are likely to be balanced on the side surfaces of fiber structure. The unbalance of the He flux flow could contribute to the one-dimensional growth of fiber structure during the He plasma irradiation. It would be difficult for He ions to impinge on the base of nanostructures after the nanostructures are grown. Only the possible channel for the growth from the base is the diffusion of He atoms and clusters to the bottom of the base through nanostructures. Although the model in this study does not deny the possibility of the growth from the base, it suggested that the nanostructures can grow even without the growth from the base.

In the initial formation process, pinholes are formed on the surface. The area of pinholes is measured from the SEM micrographs, and the number of the pinholes is counted. A fractal relation was identified between the population and the area of the pinholes. The fractal dimension was measured with different He fluences; it increased from 0.95 to 2.40 with increasing the He fluence from 0.6 to 4.7 ×10^{25} m^{-2}. When the He fluence was ∼3×10^{25} m^{-2}, the fractal dimension would correspond to that identified on the craters of the moon.

In the present case, the size and the population of pinholes are originated from He bubbles grown near the surface. Thus, it was suggested that the population of He bubbles increases with decreasing the size in accordance with a power law. Although the reason why the population distribution has fractality is not understood, it will be
of importance to investigate whether similar distribution and temporal evolution of distribution can be predicted or realized by theoretical study and simulation.

From the brightness distribution of a TEM micrograph, the fractality was identified in the scale greater than 4–5 nm and the fractal dimension was 2.65 ± 0.02. The value was in between the two different fractal dimensions observed in different scales characterized from SEM analysis previously [27], indicating that surface fractality was influenced by the inner porous structure. In addition, the fractal dimension is estimated from krypton gas adsorption isotherms. The fractal dimension (corresponds to the scale roughly less than 2 nm) decreases from 2.8 to 2.4 with increasing the He fluence. The results also indicate that the surface roughness of the nanostructure fiber has the fractality of ~2.4 in less than nanometer scale.

Although strong consistency cannot be identified between the SEM analysis, which reflects the surface morphology and was conducted previously [27], and TEM analysis, which contains the inside porous structure, the fact that the fractality and multifractality were identified in TEM micrograph suggested that the inner porous structure strongly influences on the fractal surface observed from SEM micrographs and gas adsorption property. Moreover, it is highly likely that the multifractal property identified on inner porous structure can be originated from the fractal population distribution of He bubbles suggested from the pinhole analysis. Gas adsorption property revealed the fact that the nanostructure could have fractality in the subnanometer scale. The present study could not identify the roughness in the subnanometer scale from micrographs, it is likely that the fractal roughness is formed by nano-bubbles formed just beneath the surface or reached the surface.

This work is basically dedicated to understand the growth process of the nanostructures by analyzing the detailed shape, feature, and characteristics of nanostructures. It is expected that the characterized fractality and presented properties of nanostructures are used for comparative investigation with simulation and form a bridge between experimental observation and theoretical and numerical studies to reveal un-known properties of the He bubble induced nanostructures.

Acknowledgments

Authors thank Dr M Yajima from NIFS (National Institute for Fusion Science) and Prof Y Hatano from Toyama University for providing gas adsorption isotherms data and Dr A Taguchi from Toyama University for fruitful discussion about the analysis of the adsorption isotherms. Authors also thank Dr M Tokitani from NIFS and M Miyamoto from Shimane University for useful comments about the analysis of TEM micrographs. This work was supported in part by a Grant-in-Aid for Young Scientists (A) (23686133 from the Japan Society for the Promotion of Science (JSPS), NIFS collaborative research program (NIFS1KUHR013 and NIFS13KOBF026), and NIFS/NINS under the project of Formation of International Network for Scientific Collaboration.

References

[1] Takamura S, Ohno N, Nishijima D and Kajita S 2006 Plasma Fusion Res. 1 051
[2] Takamura S, Miyamoto T and Ohno N 2012 Nucl. Fusion 52 123001
[3] Nishijima D, Baldwin M, Doerner R and Yu J 2011 J. Nucl. Mater. 415 596
[4] Kajita S, Temmerman G D, Morgan T, van Eden S, de Kruijf T and Ohno N 2014 Nucl. Fusion 54 033005
[5] Kajita S, Saeki T, Yoshida N, Ohno N and Iwamae A 2010 Appl. Phys. Express 3 085204
[6] Kajita S, Yoshida T, Kitaoka D, Etoh R, Yajima M, Ohno N, Yoshida H, Yoshida N and Terao Y 2013 J. Appl. Phys. 113 134301
[7] Komori K, Yoshida T, Yagi S, Yoshida H, Yajima M, Kajita S and Ohno N 2014 e-J. Surf. Sci. Nanotech. 12 343
[8] de Respinis M, de Temmerman G, Tanyeli I, van de Sanden M C M and De Temmerman G 2014 Interfaces 5 7621
[9] Kajita S, Ohno N, Takamura S, Sakaguchi W and Nishijima D 2007 Appl. Phys. Lett. 91 261501
[10] Kajita S, Ohno N, Hirahata Y and Hiramatsu M 2013 Fusion Eng. Des. 88 2842
[11] de Temmerman G, Bystron K, Zielinski J, Balden M, Matern G, Arnas C and Morot L 2013 J. Vac. Sci. Technol. A 30 041306
[12] Takamura S 2014 Plasma Fusion Res. 9 1405131
[13] Tanyeli I, Morot L, van de Sanden M C M and de Temmerman G 2014 ACS Appl. Mater. Interfaces 6 3442
[14] Kajita S, Kitaoka D, Ohno N, Yoshihara R, Yoshida N and Yoshida T 2014 Appl. Surf. Sci. 303-308
[15] Jyakkunulla S, Morot L, Eren B, Steiner R, Moser L, Mathys D, Dugelin M, Chapon P and Meyer E 2014 ACS Appl. Mater. Interfaces 6 11609
[16] Petty T and Bradley J 2014 J. Nucl. Mater. 453 320
[17] Baldwin M and Doerner R 2008 Nucl. Fusion 48 035001
[18] Kajita S, Yoshida N, Yoshihara R, Ohno N and Yamagawa M 2011 J. Nucl. Mater. 418 152
[19] Krasheninnikov S 2011 Phys. Scr. 2011 014040
[20] Martynyenko Y V and Nagel M Y 2012 Plasma Phys. Rep. 38 996
[21] Li X-G, Liu Y-N, Yu Y, Luo G-N, Shu X and Lu G-H 2014 J. Nucl. Mater. 451 356
[22] Takayama A, Ito A, Saito S, Ohno N and Nakamura H 2013 Jpn. J. Appl. Phys. 52 01AL03
[23] Tamura T, Kobayashi R, Ogata S and Ito A M 2014 Modelling Simul. Mater. Sci. Eng. 22 015002
[24] Krasheninnikov S, Faney T and Wirth B 2014 Nucl. Fusion 54 073019
[25] Ito A, Yoshimoto Y, Saito S, Takayama A and Nakamura H 2014 Phys. Scr. 2014 014062
[26] Ito A 2014 IAEA Fusion Energy Conf.
[27] Kajita S, Tsuji Y and Ohno N 2014 Phys. Lett. A 378 2533
[28] Ohno N et al 2001 Nucl. Fusion 41 1055
[29] Takamura S 2014 Plasma Fusion Res. 9 1302007
[30] Wright G M private communication
[31] Yajima M, Yoshida N, Kajita S, Tokitani M, Baba T and Ohno N 2014 J. Nucl. Mater. 449 9
[32] Kanda K, Fujimoto K, Uehata K, Ibano K, Tae I H and Ueda Y 2014 Characteristics of helium induced nano-structure on several refractory metals Proc. Plasma Conf. (Niigata, Japan, 2014)
[33] Galindo R E, van Veen A, Evans J, Schut H and de Hosson J 2004 Nucl. Instrum. Methods Phys. Res. 217 262
[34] Takayasu H 1986 Fractal (in Japanese) (Tokyo: Asakura Publishing)
[35] Feder J 1988 Fractals (New York: Plenum)
[36] Falconer K 2003 Fractal Geometry: Mathematical Foundations and Applications 2nd edn (New York: Wiley)
[37] Avnir D, Farin D and Pfeifer P 1983 J. Chem. Phys. 79 3566
[38] Avnir D and Jaroniec M 1989 Langmuir 5 1431
[39] Kaneko K, Sato M, Suzuki T, Fujiwara Y, Nishikawa K and Jaroniec M 1991 J. Chem. Soc. Faraday Trans. 87 179
[40] Prouzet E, Boissiere C, Kim S S and Pinnavaia T J 2009 Microporous Mesoporous Mater. 119 9
[41] Takei T and Chikazawa M 1998 J. Ceram. Soc. Japan 106 353
[42] Sefa F, Hammond K D, Justin N and Wirth B D 2013 Nucl. Fusion 53 073015