Materials Research Express

PAPER

Sputtering parameters effect on microstructural parameters of TiN coating via the Williamson-Hall analysis

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Keywords: TiN coating, sputtering parameter, Williamson-Hall, crystal size, lattice strain

Abstract

Titanium nitride (TiN) coatings were deposited on Zr-4 substrate by direct current magnetron sputtering. The microstructural property of the as-deposited coating was studied by means of x-ray diffraction (XRD). The microstructural parameters, such as crystal size, lattice strain, lattice deformation stress and lattice deformation energy density, were investigated in detail by employed modified Debye–Scherrer method (MDS) and Williamson–Hall methods by assuming three models namely uniform deformation model, uniform stress deformation model and uniform energy density deformation model. And the effects of sputtering power, substrate temperature and substrate bias on microstructural parameters were investigated. The results show that TiN coating deposited by magnetron sputtering presents lattice compressive strain, except for sample X3-1 which is prepared by substrate bias of \( \sim 50 \) V. It is also shown that sputtering power, substrate temperature and substrate bias have great influence on crystal size, lattice strain, lattice deformation stress and lattice deformation energy density of the as-deposited TiN coating. Especially the influence of substrate bias is very significant.

1. Introduction

TiN has high hardness (HV3000), good thermal conductivity (19.3 Wm\(^{-1}\)K\(^{-1}\)), high melting temperature (\( \sim 2950 \) °C), excellent corrosion resistance, wear resistance and oxidation resistance. Therefore, TiN is often used as a functional coating material in many application. Due to the excellent corrosion resistance and wear resistance, TiN as a commercial PVD hard coating, is widely used in the tools industry \[1–6\]. Also, some researchers have applied TiN to the surface coating of zirconium alloy for nuclear power \[7–11\]. The selective spectral range optical transmission and reflection properties of TiN coating make it suitable for solar cells and optical filters \[12–14\]. TiN is even used as a coating on animal organism tissues due to its excellent wear and oxidation resistance \[15\]. According to previous reports, TiN coating can be deposited by a wide variety of techniques including pulsed laser deposition technique \[6, 16\], magnetron sputtering \[10, 11, 17\], thermal spraying \[18\], cathodic arc-evaporation technique \[19\], atomic layer deposition \[20\], atmospheric pressure chemical vapor deposition \[14, 21\] and so on. It is reported that the corrosion resistance has been considered as one of the most importance properties for the materials used in the nuclear power \[22–27\]. When TiN is deposited on zirconium alloy as a protective coating, excellent corrosion resistance is very important and key. Many studies have shown that the corrosion resistance of materials is very sensitive to their microstructure \[28, 29\]. Therefore, the microstructural parameters of TiN coating such as crystal size and lattice strain should be studied in detail.

So far, various methods have been proposed to estimate the microstructural parameters. Using x-ray diffraction peak broadening, Debye–Scherrer formula can be employed to estimate the crystal size. However,
since the effect of lattice strain on the broadening of diffraction peaks is not taken into account, the crystal size calculated by Debye–Scherrer formula is often inaccurate. It is generally believed that the lattice strain is induced by vacancies, dislocations, secondary phases, impurities, mechanical deformations and thermal effects [30–33]. By considering the contribution of crystal size and lattice strain on the broadening of diffraction peaks, Williamson–Hall (W-H) method [34] can be utilized to estimate the crystal size and lattice strain. As long as the diffraction peak profile can be approximated as Cauchy/Lorentzian function, the W-H method can be used to estimate effectively. Thus, the method has been widely employed to estimate crystal size and lattice strain of nanoparticles silver [35], (BaMg0.3Al0.7O3) [36], Y2O3 [37], CoAl2O4 [38] and Ni1–xMgxFe2O4 [39].

This study is aimed to investigate the influence of sputtering parameters, such as sputtering power, substrate temperature and substrate bias, on the microstructural properties of TiN coating on Zr-4 alloy. The detailed research on several microstructural parameters of TiN nanoparticles based on x-ray peak broadening is carried out. Modified Debye–Scherrer (MDS) method and W-H method are employed to estimate crystal size, lattice strain, crystal deformation stress and lattice deformation energy density of the as-deposited TiN coating prepared by different sputtering parameters. Under different assumptions, three models based on W-H method are used, namely, uniform deformation model (UDM), uniform stress deformation model (USDM) and uniform deformation energy density model (UDEDM).

2. Experimental details

The TiN coating was deposited on Zr-4 plate by using direct current magnetron sputtering. Before the sputtering, Zr-4 plates were polished by sand paper with different mesh numbers to obtain very high surface finish. The roughness of all the pretreated substrates were located in the range of 0.1 ± 0.03 μm. After that, the substrates were ultrasonically cleaned in acetone and alcohol for ten minutes, respectively. Then, those substrates were dried and packed for using. And the dimensions of all substrates were 20 × 20 × 2.2 mm. TiN target was used. High pure argon was introduced into the chamber as protective work gas and the pressure of the argon gas was retained at about 1 Pa during the sputtering. In the chamber, the substrates were kept about 75 mm away from the target. And the substrates were placed on a homemade tooling which ensures that the substrates can rotation and revolution in the same time during the process of sputtering. With this tooling, several specimens covered uniformly by coating on both sides can be obtained in one time. The deposition time of all specimens were 10 h. And the sputtering power, substrate temperature and substrate bias of the specimens are showed in table 1.

The x-ray diffraction (XRD) patterns of the as-deposited TiN coatings were analyzed using x-ray diffractometer (D/Max 2500) with filtered Cu Kα radiation operating at 150 mA and 40 kV. The detected diffraction angle (2θ) was scanned from 20° up to 90°. The scan rate and the step size were 2°/min and 0.02°. In order to correct the effect of instrumental broadening, the XRD pattern of a fully recrystallized silicon sample was obtained by using the same equipment parameters as those of TiN coated samples.

3. Results and discussion

3.1. XRD analysis

XRD patterns of the sputtered TiN coatings prepared by different sputtering powers, substrate temperatures and substrate biases are shown in figure 1. For all the tested TiN-coated Zr-4 samples, there are four diffraction peaks related to TiN and four diffraction peaks related to Zr in the XRD pattern. This shows that the x-ray penetrates the thin TiN coating (the thickness of the coating was about 1.5 ~ 5 μm) on the surface of the specimen and reaches the internal Zr alloy. It can be found that the planes (111), (200), (311) and (222) of face-centered cubic phase of TiN were observed for all the tested samples. With standard PDF data with card number (#87–0633), the four crystal planes are observed at 2θ = 36.645°, 42.569°, 74.021° and 77.913°, respectively. From the XRD patterns, it can be found that, for the samples of X1–3, X2–3 and X3–1, the diffraction peak corresponding to the crystal plane (111) was sharp and narrow, and the diffraction intensity was the largest of all the diffraction peaks. In Group X1 and X2, the positions of four diffraction peaks corresponding to TiN did not deviate obviously.

| Group | Sputtering power (W) | Substrate temperature (°C) | Substrate bias (V) |
|-------|----------------------|---------------------------|-------------------|
| X1    | 300, 400, 500, 600   | 400                       | −100              |
| X2    | 600                  | 100, 200, 300, 400        | −100              |
| X3    | 600                  | 400                       | −50, −100, −200, −300 |

Table 1. Process parameters of TiN coatings prepared by different sputtering powers, substrate temperatures and substrate biases.
However, in Group X3, the position of diffraction peaks corresponding to crystal plane (111) for the four samples in this group were obviously shifted. Among them, the diffraction peaks of sample X3-3 were found to be shifted to the left compared with the other three samples in Group X3.

3.2. Structural characterization

Through further analysis of XRD test results, the microstructural parameters of the sputtered TiN coatings, such as crystal size, lattice strain, lattice deformation stress and lattice deformation energy density, were estimated by modified Debye–Scherrer method (MDS) and W-H method. Three models based on W-H method were
employed, that is, uniform deformation model (UDM), uniform stress deformation model (USDM) and uniform deformation energy density model (UDEDM). Four diffraction peaks that corresponding TiN (111), (200), (311) and (222) planes were selected for carrying out the W-H analysis. The mean crystalline size \( D \) and lattice strain \( \varepsilon \) were estimated assuming a Lorentzian shape for the diffraction peaks, and the total peak broadening \( \beta_{\text{full}} \) was only related to \( D \) and \( \varepsilon \).

The effect of instrumental broadening can be corrected by the following expression.

\[
\beta_{\text{full}} = \sqrt{\beta_m^2 - \beta_i^2}
\]

where \( \beta_m \) is the measured peak broadening and \( \beta_i \) is the instrumental peak broadening. With Jade software, the full width at half maxima (FWHM) plot of instrument can be established with the XRD pattern of a fully recrystallized silicon sample. Using the FWHM plot, \( \beta_i \) corresponding to any angle in the tested range can be obtained.

3.2.1. Modified Debye–Scherrer method

By employed the Debye–Scherrer method, the crystal size was calculated directly using the following relation:

\[
D = \frac{\kappa \lambda}{\beta \cos \theta}
\]

where \( D \) is crystal size, \( \kappa \) is the shape factor, \( \lambda \) is the wavelength of Cu-K\( \alpha \) radiation (\( \lambda = 0.154051 \) nm), \( \theta \) is the Bragg angle (in degree) and \( \beta \) is the peak broadening which the effect of instrument broadening has been removed. Based on equation (2), \( D \) can be calculated by using each diffraction peak in the XRD pattern and the values of \( D \) should be the same. However, in practical calculation, it is difficult to obtain the same crystal size from the parameters of each diffraction peak mainly due to a systematic error. In order to eliminate the influence of system error, equation (2) was rearranged and logarithmic operations were performed on both sides. Thus, equation (2) evolves into the following form.

\[
\ln(\beta) = \ln\left(\frac{\kappa \lambda}{\beta D}\right) + \ln\left(\frac{1}{\cos \theta}\right)
\]

Based on equation (3), the relationship between \( \ln(\beta) \) and \( \ln(1/\cos \theta) \) can be expressed as a linear function. And crystal size can be estimated according to the intercept of the linear function plot on the vertical axis. The process of estimating crystal size based on equation (3) is called modified Debye–Scherrer method (MDS) \([40, 41]\). Some typical plots between \( \ln(\beta) \) and \( \ln(1/\cos \theta) \) are displayed in figure 2. The crystal size \( D \) can be calculated by the intercept on the vertical coordinate axis. The crystal size \( D \) of TiN coatings prepared by all different process parameters calculated by MDS method were listed in tables 3, 4 and 5.

3.2.2. Uniform deformation model

It is generally believed that the broadening of diffraction peaks can be attributed to the contribution of crystal size and lattice strain. Based on this, the W-H method decomposes the total diffraction peak broadening into two parts as shown in equation (4).

\[
\beta_{\text{full}} = \beta_D + \beta_c
\]

where \( \beta_D \) represents the peak broadening due to the contribution of crystal size and \( \beta_c \) represents the peak broadening due to the contribution of lattice strain which is derived from crystal defects and distortions.

The uniform deformation model (UDM) assumes that the lattice strain in the material is uniform in all crystal phase directions. And \( \beta_D \) and \( \beta_c \) can be calculated by the following expression:

\[
\beta_D = \frac{\kappa \lambda}{D \cos \theta}
\]

\[
\beta_c = 4\varepsilon \tan \theta
\]

Thus, equation (4) can be rearranged as the following expression.

\[
\beta_{\text{full}} \cos \theta = \frac{\kappa \lambda}{D} + 4\varepsilon \sin \theta
\]

Some typical plots between \( \beta_{\text{full}} \cos \theta \) and \( 4\sin \theta \) were displayed in figure 3. Using the linear equation obtained by linear fitting shown in figure 3, crystal size \( D \) and lattice strain \( \varepsilon \) can be calculated from the interception on vertical coordinate axis and the slope of the fitted line. The crystal size \( D \) and lattice strain \( \varepsilon \) of TiN coatings prepared by different sputtering powers, substrate temperatures and substrate biases calculated by UDM method are listed in tables 3, 4 and 5, respectively.
3.2.3. Uniform stress deformation model

According to the constitutive relationship, the Young’s modulus of crystals has anisotropic nature. Therefore, the strain in the direction of each crystal phase should not be uniform. The lattice strain along the direction \([hkl]\) can be expressed as the following relation.

\[
e_{s\ hkl} = \frac{\sigma}{Y_{hkl}}
\]

where \(\sigma\) is the crystal stress, \(e_{s\ hkl}\) and \(Y_{hkl}\) are lattice strain and Young’s modulus along the direction \([hkl]\), respectively. As a result, the W-H equation was evolved to the following form.

Figure 2. MDS analysis of TiN coating prepared from (a) specimen X1-4, (b) specimen X2-3 and (c) specimen X3-1.
The W–H method based on equation (8) was called as uniform stress deformation model (USDM). Young’s modulus of cubic crystals along the direction [hkl] can be calculated by using the following equation [42]:

$$\beta_{hkl} \cos \theta = \frac{k \lambda}{D} + \frac{4 \sigma \sin \theta}{Y_{hkl}}$$  \hspace{1cm} (8)

Here $S_{11}$, $S_{12}$, and $S_{44}$ are the elastic compliances. The estimated values of elastic compliances $S_{11}$, $S_{12}$, and $S_{44}$ for TiN were $2.17 \times 10^{-12}$, $-0.38 \times 10^{-12}$, and $5.95 \times 10^{-12}$ Pa$^{-1}$, respectively [43]. Therefore, $Y_{hkl}$ of TiN along
the directions [111], [200], [311] and [222] were calculated according to equation (9) and the results were listed in table 2.

Some typical plots between $\beta_{hkl} \cos \theta$ and $4 \sin \theta / Y_{hkl}$ were displayed in figure 4. Using the linear equation obtained by linear fitting shown in figure 4, the crystal size $D$ can be determined from the interception on vertical coordinate axis and the uniform crystal stress $\sigma$ can be calculated from slope of the fitted line. The crystal size $D$ and crystal stress $\sigma$ of TiN coatings prepared by different sputtering powers, substrate temperatures and substrate biases calculated by USDM method were listed in tables 3, 4 and 5, respectively. The corresponding lattice strain $\varepsilon_{hkl}$ was plotted in figures 6, 7 and 8, respectively.

### 3.3. The influence of process parameters

#### 3.3.1. Sputtering power

The microstructural parameters of TiN coatings prepared by different sputtering powers estimated used MDS, UDM, USDM and UDEDM were listed in table 3. It is easy to find that crystal size obtained by MDS was larger than that obtained by UDM, USDM and UDEDM. This is because the contribution of lattice strain was neglected in MDS. According to the lattice strain estimated using W-H method, there were compressive strain in lattice for all the four tested samples. Thus, MDS method obtained larger crystal size than W-H method. With the increase of sputtering power, the crystal size decreased slightly. Among the three different W-H methods, the crystal size estimated by USDM model was the smallest, followed by UDEDM and UDM. Among the four samples in Group X1, the crystal size of sample X1-3 which was prepared by sputtering power of 500 W was the smallest. On the contrary, the lattice compressive strain, crystal compressive deformation stress and lattice deformation energy density of the sample were the largest.

The lattice strain along the direction [111], [200], [311] and [222] of TiN coating prepared by different sputtering powers estimated using USDM and UDEDM were plotted in figure 6. It is not difficult to find that the four crystal planes of the four samples estimated by the two methods were all in the state of compressive strain. And the lattice compressive strain estimated by USDM was larger than that estimated by UDEDM. Among the four crystal planes of each sample, the lattice compressive strain corresponding to crystal plane (200) was the smallest. Also, the four lattice compressive strains of sample X1-3 prepared by sputtering power of 500 W were found to be larger than that of the other three samples, whether estimated by using USDM or UDEDM. This was the same as the results which were estimated by UDM as shown in table 3. Moreover, the difference between the estimated lattice compressive strains of the four crystal planes of this sample was relatively large. In contrast, the difference between that of the other three samples was much smaller.

With the increase of sputtering power, on the one hand, the velocity of incident particles will increase, on the other hand, the number of incident particle per time will increase, that is to say, the deposition rate of the TiN coating will increase, which has been shown in literature [10]. The increase of the incident particle velocity means that the energy of the incident particle increases, which makes the diffusion rate of the incident particle...
deposited on the substrate higher. As a result, the probability of lattice defects and distortions is reduced. However, on the other hand, the increase of the deposition rate of the coating increases the probability of the lattice defects and distortions of the coating. Therefore, the influence of sputtering power on the lattice strain of TiN coating is a combination of incident particle velocity and coating deposition velocity. It can be concluded that this is the reason why the lattice compressive strain of the coating prepared with 500 W is the largest among the four samples. The largest lattice compressive strain makes the crystal size of TiN coating prepared by 500 W the smallest among the four samples.

**Figure 4.** USDM analysis of TiN coating prepared from (a) specimen XJ-4, (b) specimen X2-3 and (c) specimen XJ-1.
3.3.2. Substrate temperature

Table 4 lists the microstructure parameters of TiN coatings prepared by different substrate temperatures estimated using MDS, UDM, USDM and UDEDM. The estimated results show that compressive strains were found for all the four samples. Therefore, crystal size estimated by the three W-H methods was smaller than that of estimated by MDS. It is also found that the crystal size estimated by W-H method with three different models was almost the same. As shown in Table 4, the crystal size estimated by UDM model was the largest, followed by USDM and USDM. Among the four samples, the crystal size of sample X2-3 which was prepared by substrate temperature of 300 °C was the largest. On the contrary, the lattice compressive strain, crystal compressive deformation stress and lattice deformation energy density of the sample were the smallest. While, the lattice compressive strain and density of deformation energy of sample X2-1 was the largest.

Figure 7 shows the lattice strain along the direction [111], [200], [311] and [222] of TiN coatings prepared by different substrate temperatures estimated using USDM and UDEDM. Lattice compressive strain was found for all four crystal planes of the coatings prepared by four different substrate temperatures. Also, the lattice compressive strain estimated by USDM was larger than that estimated by UDEDM. And the absolute value of lattice strain of crystal plane (200) of each sample was the smallest. It is also found that no matter the USDM or USDM model was used, the estimated lattice compressive strain of the four crystal planes of sample X2-2 was the smallest of the four samples. In addition, it can be found that the lattice strains of the samples X2-2 and X2-4 were almost the same for each crystal plane no matter estimated by the USDM or UDEDM.

With the increase of the substrate temperature, the larger the activation energy of the incident particles is, the higher the diffusion rate of the incident particles on the substrate surface is. This can effectively reduce the crystal defects in the process of coating crystallization. Therefore, it can be found that when substrate temperature is from 100 °C (sample X2-1) to 200 °C (sample X2-2), and then to 300 °C (sample X2-3), the estimated lattice compressive strain decreases gradually. With the increase of substrate temperature, the mobility of ad atoms increases, which is conductive to the nucleation and condensation of grains, which leads to the increase of crystal
size and the decrease of lattice defects. Such an increase of crystal size with increase of substrate temperature has also been reported by Senthilkumar et al [44]. Therefore, it can be seen that although the lattice compressive strain of sample X2-3 is the smallest, its crystal size is the largest. The largest crystal size of the coating grown at 300°C is also an evidence of its high compaction (decreasing the grain boundaries), confirmed by the highest intensity of the diffraction peak at this temperature which is shown in figure 1(b) (the blue line). However, at very high temperatures, desorption process appears, because the adsorption energy is greater than the surface energy and the ad atoms are desorbed leading to the reduction in crystal size [45, 46]. This is the reason for that the crystal size of sample X2-4 is smaller than that of sample X2-3. In addition, it can be found that the lattice compressive strain of sample X2-4 deposited at higher substrate temperature (400°C) is larger than that of

![Figure 5. UDEDM analysis of TiN coating prepared from (a) specimen X1-4, (b) specimen X2-3 and (c) specimen X3-1.](image)
sample X2-3 deposited at lower substrate temperature (300 °C). This is in agreement with the results observed by Subramanian et al.\(^4\)\(^5\).

### 3.3.3. Substrate bias

The microstructural parameters of TiN coatings prepared by different substrate biases estimated used MDS, UDM, USDM and UDEDM were listed in table 5. It is easy to find that the crystal size of the sample X3-1 prepared by substrate bias of −50 V was significantly larger than that of the other three samples. Also, the estimated lattice strain of this sample was found to be in the state of tensile strain. Thus, the crystal size estimated by UDM, USDM and UDEDM was larger than that estimated by MDS. Moreover, it is not difficult to find that the influence of the crystal tensile strain on crystal size was very remarkable. Because the contribution of lattice tensile strain is taken into account, the crystal size estimated by the three W-H methods was more than twice as large as that estimated by MDS. The other three samples in Group X3 presented lattice compressive strain. Especially for sample X3-4, the lattice compressive strain reached −0.00401, which was much larger than that of all the other samples shown in this study. Accordingly, the estimated lattice deformation stress and lattice deformation energy density of this sample were the largest. In addition, it can be found that the lattice strain of the sample changed from tensile strain to compressive strain with the increase of the substrate negative bias, and the value increased gradually. Correspondingly, the crystal size was gradually reduced.

Figure 8 shows the lattice strain along the direction \([111]\), \([200]\), \([311]\) and \([222]\) of TiN coating prepared by different sputtering powers.

![Figure 6. Lattice strain along the direction (a) [111], (b) [200], (c) [311] and (d) [222] obtained by USDM and UDEDM for TiN coating prepared by different sputtering powers.](image-url)
strain, which was distributed in the range of $-0.0044 \sim -0.0038$. The estimated results of the four samples in Group X3 showed that the substrate bias has a significant effect on the microstructure parameters of TiN coating.

The substrate bias mainly affects the bombardment energy of the sputtered particles. Under the action of substrate negative bias, the charged particles will accelerate to fly to the surface of the substrate, which leads to the increase of the energy of the incident particles bombarding the substrate surface. This means that the larger the substrate negative bias applied, the higher energy of the bombardment of particles. In addition, the diffusion ability of high energy bombardment particles deposited on the substrate will be improved. Therefore, the crystallinity of high energy bombardment particles deposited on the substrate will be improved. Therefore, the crystallinity of high energy bombardment particles can deteriorate the crystal structure of the coating deposited on the substrate, and it will also lead to the occurrence of re-sputtering, resulting in the increase of lattice defects. In this study, the estimated crystal size of the sample of X3-1 is about 10 times of that of other samples, and shows a large lattice tensile strain. The reason may be that the negative bias applied on the substrate is relatively small, the particle energy bombarding the substrate is also relatively small. So, it can be seen from figure 1(c) that the diffraction peak related to crystal plane $(111)$ of sample X3-1 are strong and sharp. This is coincide with the large agglomerations exhibit on the surface of TiN coating prepared by $-50$ V substrate bias as described in the literature [11]. The estimated results show that the sample of X3-4 which is prepared by substrate bias of $-300$ V exhibits a large lattice compressive strain. This may be due to the occurrence of re-sputtering caused by excessive substrate bias, which leads to the increase of lattice defects.

4. Conclusions

TiN nanoparticle coatings were deposited on Zr-4 alloy by direct current magnetron sputtering with different sputtering parameters. XRD was used to characterize the microstructure of as-deposited coatings. MDS and the three models based on W-H method were employed to estimate the microstructural parameters such as crystal
size and lattice strain. And the influence of sputtering power, substrate temperature and substrate bias on the microstructural parameters was studied. Some conclusions were drawn as following:

1. The TiN coating deposited on Zr-4 alloy by magnetron sputtering presents a crystalline state. The results of W-H analysis show that there was lattice compressive strain in the as-deposited coating, crystal size range was between 8.68–15.61 nm, except for sample X3-1. Due to the existence of lattice compressive strain, the crystal size estimated by MDS method was larger than that estimated by W-H method.

2. Sputtering power, substrate temperature and substrate bias had great influence on the microstructural parameters such as crystal size, lattice strain, lattice deformation stress and lattice deformation energy density of TiN coating. Especially the influence of substrate bias was very significant. Among them, the sample prepared by substrate bias of −50 V presented lattice tensile strain, which was the only sample with tensile strain in this study, and its crystal size was also the largest one among all the studied samples. Moreover, the estimated lattice compressive strain of samples prepared by −300 V substrate bias was the largest of all the samples studied in this paper.

The corrosion resistance is very importance to the coating for Zr-4 alloy. And the corrosion behavior of the coating is very sensitive to their microstructural parameters. This study showed that process parameters affect significantly on the microstructural parameters of the as-deposited TiN coating. The results indicated that TiN coating with suitable crystal size and lattice compressive strain can be obtained by using magnetron sputtering with sputtering power of 600 W, substrate temperature of 400 °C and substrate bias of −100 V.

Figure 8. Lattice strain along the direction (a) [111], (b) [200], (c) [311] and (d) [222] obtained by USDM and UDEDM for TiN coating prepared by different substrate biases.
Acknowledgments

This work was supported by Operation Fund of Key Laboratory for Nuclear Reactor System Design (HT-KFKT-10-2018002), Natural Science Foundation of Hunan Province of China (2020JJ5467) and Scientific Research Foundation of Hunan Provincial Education Department (19B492, 18A240). The authors are grateful to other participants of the project for their cooperation.

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