Evaluation of tritium trap effect produced by high energy proton irradiation in SS316

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Based on results of tritium measurement in the SS316 specimens irradiated up to 5.9 dpa in the SINQ target (580MeV proton) using a thermal desorption (TDS) method, trap site density and trap energy in the materials induced by the high-energy proton irradiation have been evaluated by means of the numerical tritium transport analysis. The results indicate that almost residual tritium in the SS316 specimen exists in the trap site, whose trap density is maximum 238appm (5.9dpa) and trap energy is >1.4 eV, and that tritium release by the TDS is mainly attributed to the disappearance of the trap sites by the specimen heating, whose activation energy is about 0.7 eV. The trap site density seems to be almost proportional to the irradiation dose (dpa). Additionally, irradiation conditions such as the dose or irradiation temperature do not affect on the trapping mechanism.

Keywords: Tritium, Trap site, Irradiation, SS316, spallation, diffusion

1. Introduction

Tritium transport in irradiated materials is one of interests for the accurate tritium inventory or tritium permeation evaluation in a nuclear fusion reactor or an accelerator-driven nuclear transmutation system. As to the post irradiation experiment of high-energy irradiated materials, there are some extensive studies for the gas analysis such as hydrogen isotopes and helium in the materials irradiated with 580 MeV protons at SINQ [1, 2] target and 800 MeV proton at LANCE target [3, 4]. The authors also have measured tritium in the stainless steel 316F (SS316) irradiated in the SINQ target using a thermal desorption spectroscopy (TDS) method with a constant ramp rate [5]. The results indicated that residual tritium amount in the irradiated SS316 was less than 20% of estimated tritium generation amount by the spallation reaction in SS316. While this result agreed with the previous studies of the results of hydrogen [2, 3], the details of mechanism of residual tritium in SS316 were not clear. In order to understand such tritium retention in the irradiated SS316, the numerical tritium transport analysis based on the one-dimensional diffusion and trapping model has been performed not only for the TDS experiment but also for the high-energy proton irradiation and storage period. This paper presents the results of a numerical analysis on the tritium retention and release behavior in/from the irradiated SS316 obtained by the TDS experiments, and discusses on the tritium trapping and release mechanism and its dose effect.

2. Experimental results

Specification of the specimens, experimental procedure of tritium measurement in SS316 has been described in a previous report [5]. We recall some key data, which are closely related to the tritium transport analysis. Fig. 1 shows the schematic drawing of the tritium measurement apparatus. The tritium is extracted from specimens by the TDS method with the constant ramp rate of 10 K/min. under the gas flow (N_2+H_2(<2vol.%), 250 cm^3/min.). Tritium released from specimen is measured by an ion chamber (1.5L volume) continuously during the TDS experiment for the real time tritium measurement. Water bubblers collect all tritium
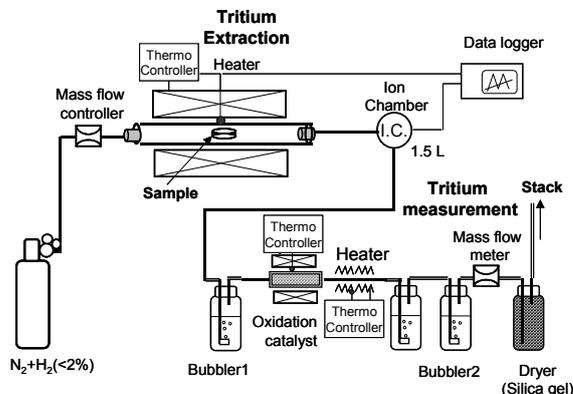
Fig.1. Schematic drawing of tritium measurement apparatus.

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extracted from the specimen for quantitative measurements remained in the specimen.

Table 1 summarizes the specification of the specimens and results of the tritium measurement. The specimens used for tritium measurement were three discs of SS316 (3mm in diameter, 0.2mm in thickness and 13mg of a weight) irradiated 5 dpa at 363-383 K and 5.9 dpa at 383-433 K, respectively. Before the TDS, only #3 disc was polished by an emery paper in order to remove the effect of surface oxide on TDS behavior of tritium. Based

Table 1 Summary of specification of the specimens and the results of tritium measurement [5]

Specimen number		#1	#2	#3 (Polished)
Dose (dpa)[a]		5.9	5.0	5.0
Irradiation temp, K [b]		433/463	363/383	363/383
Evaluation	T, appm Generated T (*G*)	39 (8.6 MBq)	33 (7.3 MBq)	33 (7.3 MBq)
	H, appm	2532	2145	2145
	D, appm	150	127	127
	[4]He, appm	255	216	216
Experiment	Residual T[c]	1.37 MBq	0.91 MBq	0.87 MBq
	Residual T(*R*) [d]	1.75 MBq	1.16 MBq	1.11 MBq
R/G (%) of T		20	16	15

(a) and (b) were evaluated at PSI. (c) is measured values at a time of 1280th cooling day. (d) is estimated values at a time after irradiation.
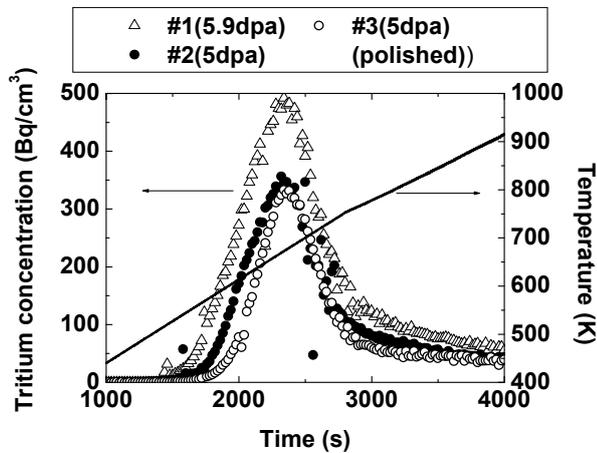
Fig.2. Tritium release behavior from the proton irradiated SS316 specimens (#1 ~ #3) (Ramp rate: 10 K/min., carrier gas: N$_2$-2vol.%H$_2$, flow rate: 250 cm^3/min.)

on the measured residual tritium amount (*R*) and the calculated tritium generation amount (*G*), the *R/G* ratio are evaluated, and those are found to be 15~20% as shown in Table 1.

Fig. 2 shows a tritium release behavior from the SS316 specimens (#1 ~ #3) obtained by the TDS. The left and right vertical axis means the tritium concentration in the carrier gas measured by an ion chamber, and specimen temperature, respectively. Tritium release from the SS316 specimens starts above 523 K, and achieves a peak at about 673K, and additional tritium release is not observed above 673 K for all specimens. A tritium release at different irradiation conditions such as #1 (5.9dpa) and #2, 3 (5 dpa) shows almost similar behavior except tritium concentration in the carrier gas. Therefore, it can be concluded that the starting and peak temperature of tritium release do not depend on the irradiation temperature. Additionally, little difference was observed between #2 and #3. So, it is concluded that the surface conditions such as oxide layer does not affect the TDS behavior, and that tritium is not maldistributed in the oxide layer of the SS316 specimen.

3. Tritium transport analysis

In order to understand observed tritium retention and tritium release behavior in/from the SS316 specimens, a numerical tritium transport analysis has been carried out. In this transport, one-dimensional diffusion equation analysis with trap effect of tritium and other hydrogen isotopes (protium and deuterium, protium represented deuterium in this analysis) in SS316 was considered using TMAP code, which was developed by Idaho National Engineering Laboratory in USA [6]. In the transport analysis, hydrogen isotopes transport can be expressed in the eqs. (1) and (2),

$$\frac{\partial C_{Ti}(x,t)}{\partial t} = \frac{D_i}{\lambda^2} C_i(x,t)\left(C_{T0} - \sum_i^n C_{Ti}(x,t)\right) - \nu_0 C_{Ti}(x,t)\exp\left(-\frac{E_T}{kT}\right) \quad (1)$$

$$\frac{\partial C_i(x,t)}{\partial t} = -D_i\frac{\partial^2 C_i(x,t)}{\partial x^2} - \frac{\partial C_{Ti}(x,t)}{\partial t} + S_i(x,t) \quad (2)$$

where, *C*: mobile concentration, C_T: trapped concentration, C_{T0}: trap site density, *S*: source, *D*: diffusivity, λ: lattice constant, ν_0: lattice vibration frequency, *k*: Boltzmann constant, *T*: temperature and E_T: trap energy for hydrogen isotopes i (T and H), respectively. Here, E_T consists of activation energy of diffusion and binding energy of hydrogen isotopes and trap site [5]. Since it is found that surface oxide does not act as the tritium release barrier in the results of #2 and #3 specimens, hydrogen isotope transport in the oxide layer is not considered in this analysis. Boundary condition at the surface is expressed in the Eq. (3) assuming the Sievert's law,

$$C(0,t) = C(d,t) = Ks_i\sqrt{P_i} \quad (3)$$

here, Ks and P means Sievert's constant, and partial pressure of hydrogen isotopes i, while d means the thickness of the specimen.

The transport analysis has been performed for the high-energy proton irradiation at SINQ and storage (irradiation phase), and the TDS after irradiation and storage of the specimens (TDS phase).

In the irradiation phase analysis, the transport analysis of hydrogen isotopes in SS316 was carried out under the tritium and hydrogen generation in SS316 by the spallation reaction, which is given by the SINQ target irradiation conditions [2]. Table 2 summarizes key parameters for this analysis such as transport properties or generation rate of hydrogen isotopes and so on [7, 8]. Fig. 3 also shows time evolution of the specimen temperature and generation rate of tritium and protium in

Table 2 Transport properties in SS316 and analytical conditions for the transport analysis

Transport properties		Value
Diffusivity (D_H) (m²/s) [7]		$D_0=1.6\times10^{-6}$
		$E_D=52.9$ kJ/mol
Diffusivity (D_T) (m²/s)		$D_0=1.6\times10^{-6}/\sqrt{3}$
		$E_D=52.9$ kJ/mol
Sievert's constant [8]		$K_{S0}=2.57\times10^{23}$
(atoms/m³-√Pa)		$E_S=0.14$ eV
v_0		1.0×10^{13} /s
λ		2.8×0^{-10}m
S (atoms/s/m³) (irradiation phase)	H	$7.3\times10^{18}/8.9\times10^{18}$
(Normal beam/Focused beam)*	T	$1.6\times10^{17}/1.9\times10^{17}$
S (atoms/s/m³) (TDS phase)		0 (H,T)
Irradiation temperature (K)		383/433 (#1)
(Normal beam/ Focused beam)*		363/383 (#2, #3)

* Normal beam operation: 0-176th and 267- 483rd day,

Focused beam operation: 484-547th day
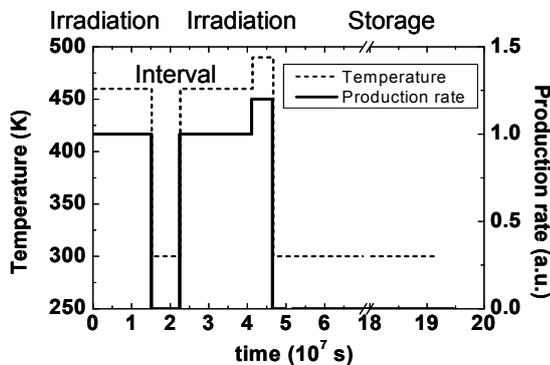
Fig. 3. Analytical conditions of the irradiation phase analysis. (H,T production rate and irradiation temperature during proton irradiation)

SS316 normalized by that at normal beam irradiation shown in Table 2, respectively for #1 specimen. Here, proton irradiation was carried out for about 1.5 years with an interval of about three month, and the specimens were stored for about four years after the proton irradiation. While actual specimen temperature and generation rate were fluttered due to the frequent beam interruption, averaged constant values were assumed in this analysis. Trapping parameters such as trap site density and trap energy were evaluated by fitting between the analytical results and the experimental result of residual tritium amount (**R/G**) in the specimens.

On the other hand, the TDS analysis was carried out under the initial condition of hydrogen isotopes distribution in the specimens derived by the irradiation phase analysis, and basic diffusion equation and boundary conditions were same with the irradiation phase analysis (eqs. (1) and (3)) except trapping effect in the specimens. The trapping parameters were also evaluated by fitting the analytical results with tritium release behavior from the specimens. We attempted two TDS mechanisms to explain observed tritium release behavior; one is tritium release by a de-trapping from the trap site shown in the eq. (2) (de-trapping model), and another is tritium release by the disappearance of the trap site by annealing of the specimen as shown in the eq. (4) (trap site anneal model).

$$\frac{\partial C_{T0}(x,t)}{\partial t} = -C_{T0}(x,t)\alpha \exp(-\frac{E_F}{kT}) \tag{4}$$

here, α and E_F means pre-exponential factor and activation energy of trap site annealing, respectively.

4. Analytical results and Discussion
4.1 The de-trapping model analysis

Fig.4 shows the analytical results evaluated by the de-trapping model for the TDS behavior compared with the experimental results. Here, (a) and (b) shows the results for the 5 dpa irradiated specimens (#2 and #3) and 5.9 dpa irradiated specimen (#1), respectively. In Fig. 4(a), the result of TDS analysis with the trap energy of 1.1 eV and the trap site density of 245 appm shows almost same tritium release peak temperature around 670 K, and the residual tritium amount in the specimen in this analysis is almost same with the experimental results (~0.9 MBq). Oliver et al. reported the trap energy of 1.1 eV in the proton irradiated 316SS up to ~20 dpa [9].

Although derived trap energy is similar to their value, this analytical result indicates that tritium release starts at lower temperature (~400K) than the experimental result (~500K) and the TDS peaks are broader than the experimental result. The difference could be attributed to the assumption of the hydrogen isotopes transport in SS316 during the proton irradiation phase. As to the results for the #1 specimen, analytical result with the trap energy of 1.1 eV at the trap site density of 350 appm
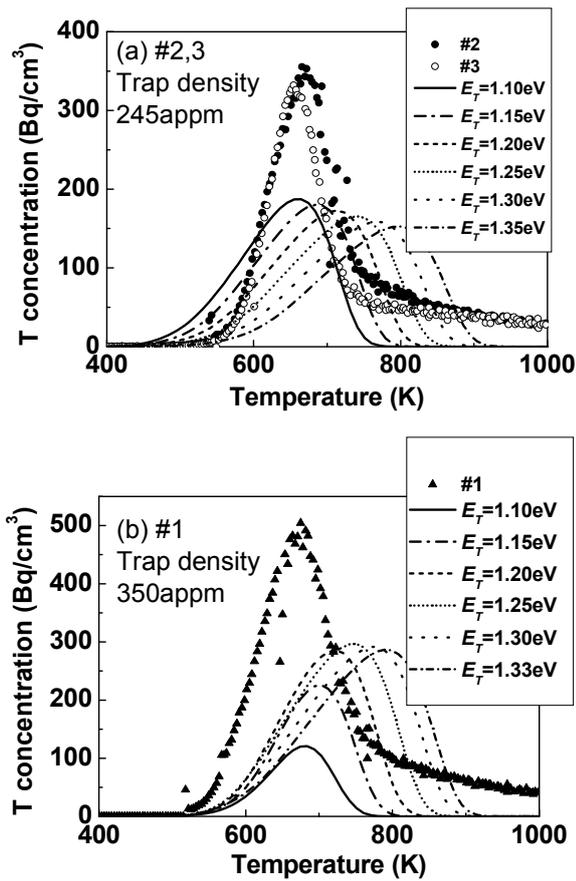
Fig. 4. Fitting results of the TDS analysis for the SS316 specimens using the de-trapping model. Where, (a) and (b) show the fitting results for #2, 3 specimen and #1 specimens, respectively.

shows that the TDS peak temperature is also almost same with the experimental result as well as the #2 and #3 specimen as shown in Fig. 4 (b). Here, the trap site density of 350 appm is just a trial value under the assumption of proportionality between the dose and the trap site density. But, this result can not satisfy the residual tritium amount in the specimen, since the derived residual tritium amount is ~0.7MBq, which is smaller than the observed value (~1.4MBq). Derived analytical results for the #1 specimen are attributed to the higher irradiation temperature than that of the #2 and #3 specimens. Since a part of tritium trapped in the trap sites should be de-trapped and released from the specimen during the proton irradiation due to the higher irradiation temperature, the residual tritium amount in the #1 specimen could be smaller than that in the #2 and #3 specimens irradiated lower temperature under the same trap site condition. When we assume over thousands appm of the trap site density in the #1 specimen, residual tritium amount will be satisfied by the de-trapping model and the experimental results. But such assumption is not reasonable, and inconsistency of the TDS peak shape still remains. Therefore, application of the de-trapping model to observed TDS behaviors is concluded to be

difficult, since we could not obtain consistent trap energy, trap site density and TDS behavior using the de-trapping model.

4.2 The trap site anneal model analysis

Prior to the trap site anneal model analysis, we obtained the *R/G* ratio and the mobile/trapped ratio of tritium in the irradiated SS316 specimens after the irradiation phase with the de-trapping model. Fig. 5 shows the *R/G* ratio in specimens for different trap site densities induced by the irradiation for the trap energy of 1.4eV derived from the transport analysis under the conditions shown in Fig. 3 for each specimen. Where, 1.4 eV of the trap energy is determined by the tritium release starting temperature of the TDS behavior on the basis of the results of the de-trapping model analysis as shown in Fig. 4(a). Those results indicate that almost tritium remained in irradiated SS316 is trapped in the trap sites, since the derived mobile/trapped ratio of tritium in the specimen is negligibly small. It is why mobile tritium in the specimen had diffused to the surface
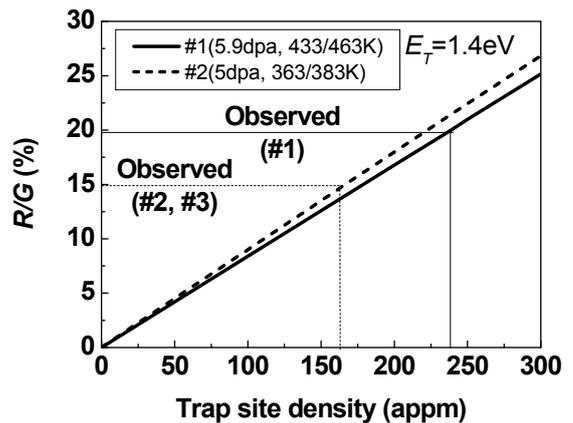
Fig. 5. *R/G* ratio in specimens for different trap site densities induced by the proton irradiation.
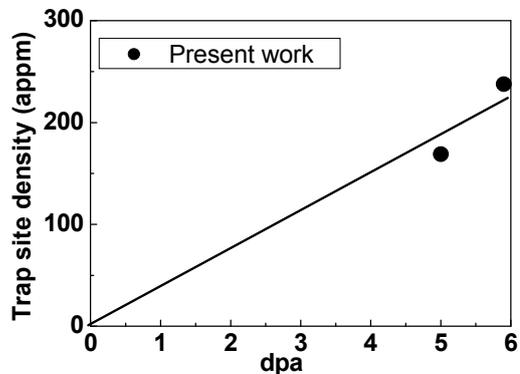
Fig. 6. Relationship between derived trap site density and irradiation dose by the irradiation phase analysis.
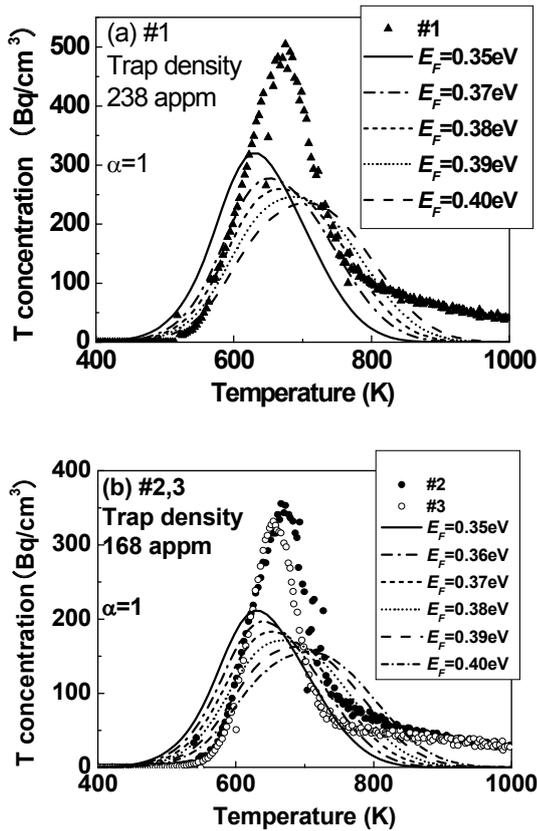
Fig. 7. Fitting results of the TDS analysis for the SS316 specimens using the trap site anneal model for α=1. Where, (a) and (b) show the fitting results for #1 specimen and #2,3 specimens, respectively.

Fig. 8. Fitting results of the TDS analysis for the SS316 specimens using the trap site anneal model for α=500. Where, (a) and (b) show the fitting results for #1 specimen and #2,3 specimens, respectively.

enhanced by heating of the specimen during proton irradiation, and had been released from the specimen. Derived trapping parameters for the #1 specimen (5.9dpa) and #2, 3 specimens (5dpa) are C_{T0} of 238appm and 168appm with E_T >1.4 eV, respectively. Fig. 6 shows the relationship between the irradiation dose of the specimens and the C_{T0}. Almost proportional relationship between the dose and C_{T0} can be seen.

In the TDS phase analysis, the trap site anneal model shown in the eq. (4) has been attempted to the explanation of the TDS behavior shown in Fig. 2. Here, initial distributions of tritium and hydrogen in the specimens are based on the results of the irradiation analysis, those are C_{T0}=238appm (#1) and 168appm (#2 and #3). Fig. 7 and Fig. 8 shows the fitting results of the TDS analysis using the trap site anneal model assuming α=1 and α=500, respectively. Here, (a) and (b) shows the results for the 5.9 dpa irradiated specimen (#1) and 5 dpa irradiated specimens (#2 and #3), respectively. The results in Fig. 7 indicated that assumption of α=1 is not suitable for the TDS mechanism. On the other hand, assumption of α=500 gives good agreement between analytical results and experimental results as shown in Fig. 8. Derived TDS behavior of E_F =0.69 eV

associated with α=500 gives good agreement with the experimental results for all specimens. Additionally, released tritium amount from each specimen well agrees with the analytical result. This result indicates that 500 hydrogen isotopes atoms are occupied in one trap site. When we assume that hydrogen isotopes is trapped in the bubbles or voids in SS316, the mean void size corresponds to about 10 nm. According to the report by Garner et al. [10], hydrogen exists as voids, whose mean size are 37-170 nm, in the stainless steels irradiated in a fast neutron reactor up to 17.5 dpa. Therefore, there is a possibility that voids or bubbles in irradiated SS316 of the hydrogen isotopes acts as trap sites which is annealed at high temperatures, although the observed and analysis could be applied to limited irradiation conditions.

On the basis of the results of the tritium transport analysis in the SINQ irradiated SS316 specimens, tritium behavior such as retention or TDS in/from irradiated SS316 can be considered as follows; (1) almost residual tritium in the SS316 specimens after irradiation exists in the trap site, whose trap energy is >1.4 eV, (2) tritium release from the specimens by the TDS is mainly attributed to the disappearance of the trap sites by annealing, and its activation energy is about 0.7 eV. Once trap site disappeared, 500 of hydrogen isotopes

atoms will be de-trapped. Therefore, we can estimate the feature of the trap site produced by the high-energy proton irradiation in the SS316 specimens as follows, although observed results can be applied to limited irradiation conditions:

(1) Single kind of trap site exists in the SS316 specimen, even though the irradiation conditions are different, since the trap energy is independent of the dose and the irradiation temperature.

(2) The trap site density increases almost linearly with the irradiation dose.

(3) Although the trap energy of the trap site induced by the irradiation in the SS316 specimens is relatively high (~1.4 eV), the trap sites will disappear in lower temperature by annealing.

(4) A possibility of bubbles as the trap site could be estimated, because the 500 of hydrogen isotopes atoms were de-trapped once a trap site disappeared.

There is still an issue on description of the irradiation defects as trap site. Further study on the relationship between production and disappearance of the irradiation defects and release behavior of tritium or other gases from the irradiated materials is desired.

5. Summary

The trap site density and trap energy in SS316 irradiated in the SINQ target (580MeV proton) up to ~6 dpa have been evaluated by the numerical analysis for the TDS behavior of tritium from the irradiated SS316. The results indicated that all of residual tritium in the SS316 specimens is trapped in the trap site, whose trap energy is >1.4 eV, and tritium release by the TDS is mainly attributed to the disappearance of the trap sites by the specimen annealing at the TDS, and its activation energy is about 0.7 eV. Additionally, it is estimated that single kind of trap site exists in the SS316 specimen even though the irradiation conditions is different, since the trap energy is independent of the dose and irradiation temperature, and the trap site density increases linearly with the irradiation dose (dpa) (238appm at 5.9 dpa).

Acknowledgement

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