Irradiation Influence on Swelling and Corrosion Behavior of ADS Beam Window Materials, T91 Steels, in Lead Bismuth

Nariaki Okubo and Yuki Fujimura

Nuclear Science and Engineering Center, Japan Atomic Energy Agency, Tokai, 319-1195, Japan

*E-mail: okubo.nariaki@jaea.go.jp
(Received September 26, 2019)

In an accelerator driven system (ADS), the beam window material of spallation neutron target will be heavily irradiated under severe conditions, where the displacement damage and high concentrations of helium and hydrogen atom accumulation in the material will occur simultaneously due to high energy spallation neutron and/or proton irradiations in the lead bismuth flow. A main materials issue dedicated to the ADS is the compatibility with the liquid metal of lead bismuth eutectic (LBE), such as liquid metal embrittlement (LME) and liquid metal corrosion (LMC). In this study, we address firstly the swelling behavior of the beam window materials, which is also important for the fuel claddings and connected indirectly with the oxidation reaction induced during irradiation or/and by the irradiation damage. Secondly, the LMC after ion irradiation of ferritic/martensitic steels, T91, are also addressed in the cases of self-ion irradiation and simultaneous irradiation with He and H atoms. The irradiations were performed at temperatures from 350 to 550°C up to 10 - 40 dpa. In the case of single ion irradiation (only displacement damage), no cavities were observed, but in the cases of dual and triple ion irradiations, many cavities were formed and caused swelling. It was concluded that helium and/or hydrogen enhanced the swelling induced by the simultaneous irradiation case and the peak swelling behavior appeared at an irradiation temperature around 450°C. It was found that, under simultaneous triple ion beams (Fe+He+H), H atoms affected significantly on the swelling development process. Comparing with the dual beams (Fe+He), the enhancement of cavity growth in the deeper region and the suppression of the growth in the medium depth region with changing the number density distributions of cavities might be caused by a fast diffusion of hydrogen atoms. From this result it can be concluded that the swelling of T91 steel depends on the implantation rates of He/dpa and H/dpa. The initial study was originally performed on LMC of T91 steels using the specimen irradiated at 450°C. After the corrosion test at 450°C in the LBE with low oxygen concentration, the surface of the triply irradiated area was covered by the oxide layer even though the non-irradiated area didn’t show the enough oxide formation. Therefore, it is concluded that the irradiation can enhance the oxide layer formation supposed due to the two reasons of (1) enhancement of Fe diffusion caused by reducing activation energy of Fe atoms due to helium-vacancy complexes and vacancy clusters after the ion irradiation and (2) enhancement of O interstitial diffusion by radiation defects.

KEYWORDS: Accelerator Driven System (ADS), Beam window, Triple Ion irradiation, Liquid Metal Corrosion (LMC), T91 steel, Lead Bismuth Eutectic (LBE)
1. Introduction

After the accident in Fukushima 1st nuclear power plants, concern increased on how to reduce the risk of many spent fuel elements, especially in Japan. An Accelerator Driven System (ADS) is one of the important concepts to realize partitioning and transmutation technology [1]. In an ADS, the beam window, which is the essential boundary between a high energy accelerator for protons in vacuum and a spallation target of Lead-Bismuth Eutectic (LBE), will be irradiated under the severe conditions to transmute sufficiently the minor actinides filed in the fuel. The ADS irradiation conditions include considerable displacement damages, and high concentrations of He and H atoms will be produced simultaneously by high energy proton and spallation neutron irradiations. Degradation of the mechanical and corrosion properties and component volume changes (swelling) after irradiation at relatively high temperature, e.g. from 450 to 550°C, should be maintained within a range permissible for the system design [2]. High fluence neutron irradiation experiments up to about 20 and 100 dpa (displacement per atom), which are estimated as the upper limits of the irradiation damage for the beam window and cladding materials [2], respectively, are practically difficult due to the long time irradiation. In particular, nuclear transmutation gas concentrations obtained in present experimental reactor irradiations are not sufficient for estimating the effects of He and H gas of ADS irradiation condition. By using boron doping techniques, in which $^{10}$B(n,α)$^7$Li reaction generates He atoms in the material under neutron irradiation, the He concentration can be achieved to the ADS condition of 50-100 appmHe/dpa [3,4]. However, the burnup of the boron is fast and could be useful only for several dpa levels. It’s difficult to get simultaneous H generation rate of 100 appmH/dpa with the He production under displacement damages even by using the spallation neutron source as a SINQ facility in PSI [5] and also difficult to control correctly the irradiation temperature because of frequent beam trips. Simultaneous multiple ion irradiation is a powerful technique for simulating ADS irradiation conditions under the accurate temperature control in order to understand the mechanism of microstructural evolution, mechanical properties by using nano-indenteter and select candidate materials prior to building the ADS material irradiation experimental facility [6]. Especially in the ADS, oxygen control technique is very important and the control system needs to be installed properly in the LBE coolant system. The oxygen concentration of LBE must be controlled below the upper concentration of lead oxide (ex. PbO) formation, which causes stuck valves and plugging the narrow flow channels of LBE after long term operation. On the other hand, in the case of ferritic/martensitic steels, ex. T91, the surface protective layer of iron oxide (ex. Fe$_3$O$_4$) dissolves in the case of lower oxygen concentration. Acceptable oxygen concentration, which depends on the LBE temperature, is ranged from $10^{-3}$ to $10^{-5}$ wt% in the case of 450°C [7]. These upper and lower oxygen concentrations are critical values of the oxygen-concentration boundary to be controlled in the ADS. The material corrosion behavior in the LBE has been studied about two decades [8, 9] and the corrosion kinetics of T91 was discussed [10]. But, only a few studies [11, 12] evaluating irradiation influence on the material properties after the neutron irradiation in LBE have been conducted from the view point of liquid metal embrittlement (LME), not from the liquid metal corrosion (LMC) for irradiated materials. In this study, the first objective to examine and evaluate the swelling and hardening behavior of ferritic/martensitic steels (FMS), T91, in the cases of
simultaneous irradiations with self-ions, helium and/or hydrogen ions at relatively high temperatures over 350°C. Secondly the influence of irradiation with ADS conditions for the materials, T91, on the corrosion was experimentally simulated by using multiple ion beam irradiation and the ex-situ corrosion in static LBE pot.

2. Experiments

2.1 Ion irradiation and microstructural observation

In the ADS, one of the candidate materials for a beam window and fuel cladding is so-called Mod.9Cr-1Mo (T91) steel. The material compositions of T91 steel is shown in Table 1. The T91 steel was normalized at 1050°C for 60 min. and tempered at 750°C for 60 min. followed by each air cooling. The specimen size was 6 mm in width, 3 mm in height and 0.75 mm in thickness. After cutting this size, the surface for ion irradiation was mechanically polished to a mirror finish and then electro-polished.

Table 1. Chemical compositions of T91 steel (wt.%).

| Fe  | Cr  | Mo | Mn | Si | V  | Ni | Nb | O   | C  | N  | W   |
|-----|-----|----|----|----|----|----|----|-----|----|----|-----|
| Bal.| 8.55| 0.94| 0.39| 0.42| 0.21| 0.02| 0.08| 0.0026| 0.096| 0.042| <0.01|

Simultaneous ion irradiation experiments have been conducted in TIARA (Takasaki Ion Accelerators for Advanced Radiation Application) of QST (National Institutes for Quantum and Radiological Science and Technology), Japan. Irradiations using 10 MeV-Fe\(^{3+}\), 1.05 MeV-He\(^+\) and 0.38 MeV-H\(^+\) ions were proceeded for T91 specimens at 350, 450, 500 and 550°C. The irradiation area was 2 by 2 mm\(^2\) for the estimation of the swelling and micro-hardness, and 10 mm\(^2\) for the corrosion tests. Experimental conditions were determined using the SRIM code [13]. The damage depth profile is shown later, in Fig. 5. The helium and hydrogen implantation rates in this experiment were about 15 and 150 appm/dpa at 1.2 μm in depth, respectively. These values were estimated by using PHITS code [14] assuming with the irradiation conditions from the LBE target in 1\(^{st}\) ADS, ex. 1 GeV proton energy, 20 mA/cm\(^2\) flux and the 2 mm thickness beam window made of T91 [2]. Depth distributions of He and H were individually broadened using by energy degraders with 800 nm thick aluminum foils, which rotated between +20° and +70° relative to each the He and H beam direction. The labels of single, dual and triple refer to only Fe, Fe+He and Fe+He+H co-irradiation, respectively. The specimen temperature was controlled by using both electron bombardment and heater, and monitored by using thermocouples and 2D infrared pyrometer, which temperature value was previously correlated by both thermocouple welded on the specimen and the pyrometer at each irradiation temperature. After the irradiation, the micro-hardness was measured by using a nano-indentener (Elionix ENT-1100a) with constant indentation depths of 400 nm at 10 points with 20 μm distance from each irradiated and non-irradiated, masked area. The swelling behavior was estimated from microstructures observed by using cross sectional Transmission Electron Microscopy (TEM, JEOL JEM-2100) operated at 200 kV. The specimen for TEM observation was picked up from surface to around 2 μm in depth using an FIB (Focused Ion Beam, Hitachi High Tech Science SMI3050SE). The specimen surface damage layer induced by FIB using the 30 keV Ga ions, was removed using flash polishing for 0.01 sec at 20 V in 20 % H\(_2\)SO\(_4\) and 80 % Methanol below 4°C.
2.2 Corrosion test in LBE

In the cases of corrosion tests, irradiated region of the specimen was half covered by aluminum foil to make non-irradiation area ether on the same specimen and the same temperature history under ion irradiation and soaking in LBE. The specimen surface for corrosion test in LBE was mechanically polished and finished by buffing using 50nm alumina nanoparticles. The irradiation and corrosion temperature was fixed at 450°C because the ADS component temperature aimed for 450°C [2] and the swelling temperature showed maximum temperature at 450°C as shown in later results. The multiple ion beam irradiation energies were already shown in Sec. 2.1. Displacement damage for corrosion tests were determined to be about 4 and 8 dpa at the specimen surface. Specimen was irradiated up to 8 dpa at surface and 20 dpa around 1 μm in depth, where He and H was co-irradiated with ratios of 15 appm He/dpa and 150 appm H/dpa, at 450°C. After ion irradiation, the specimen was soaked at 200 °C in the static pot made of silica glass with 1000 cc LBE, with fixing by using the stainless steel (SS) wire connected to a tungsten weight and the corrosion test started to count up at 450°C ±5°C, measured by thermocouple (T_C), after increasing LBE temperature. Experimental setup of the corrosion test is shown in Fig 1. The oxygen concentration in LBE was measured by using the Pt/Air type-6YSZ (Yttria Stabilized Zirconia, Y_2O_3/ZrO_2 = 6/94 (mol)) oxygen sensor fabricated by JAEA [15] and maintained by using covering gas of pre-mixed Ar+4.5%H_2 at conditions of low oxygen concentration from 10^{-8} to 10^{-9} wt%, which was around the critical low concentration of the oxide formation, Fe_3O_4 and FeO [7]. In the values of electro motive force (EMF) of the oxygen sensor, 1.00 and 1.09 V denote 2.3×10^{-8} and 1.3×10^{-9} wt% oxygen concentration in LBE at 450°C, respectively [15]. It is noted that below 10 % of the first duration of soaking time shows high oxygen concentration due to opening of the pot to set the specimens as shown in Fig.2 (a) in the case of 381 hour corrosion test. Also, as shown in Fig.2 (b) in the case of 1000 hour corrosion test, about first 15 % of...
the total corrosion time has been relatively high oxygen concentration because of using a new LBE in this experimental setup. It is not shown in this Figure, but the corrosion test was also done under the saturated oxygen concentration of constant at 2.4x10^{-4} wt% 450°C. The LBE on the surface of the specimen was cleaned up by using silicone oil at 200°C to melt down the LBE in the oil bath. To identify the oxide layer X-ray diffractometry (XRD, MAC Science MXP3 with Cu Kα X-ray source) was performed after the corrosion test. The surface morphology and cross sectional corrosion behavior were evaluated by using a Field Emission Scanning Electron Microscope (FE-SEM, ZEISS Sigma) at the accelerate voltage of 30 kV after fixing in resin, polishing to be mirror surface and depositing a few nm Os coating to avoid charging up. Energy Dispersive X-ray Spectroscopy (EDS) was conducted also to get the line analytical data and the mapping images of material elements.

3. Results and Discussions

3.1 Swelling and hardening behavior

The swelling behavior of F82H, which is a FMS similar with T91, was systematically reported by Wakai, et al. [16, 17] from the view point of fusion irradiation conditions. Here, the swelling behavior is reported for some dedicated cases of ADS irradiation conditions. Figure 3 shows cross sectional TEM images of single, dual and triple irradiated specimens, taken from the area between the 1.0 μm (lower side of the picture) and 1.6 μm (upper side of that) in depth from the irradiated surface. The irradiation damage, He and H implantation ratio was 40 dpa, 15 appm He/dpa and 150 appm H/dpa, respectively. The irradiation temperature was controlled at 500°C, which was chosen from feasibility study for ADS [2]. In the case of single ion irradiation, no cavities were observed at a displacement damage of 40 dpa around 1.2 μm in depth (even at 100 dpa, which corresponds to the peak value of nuclear energy deposition around 2 μm in depth). In the cases of dual and triple irradiations, however, many cavities appeared and

![Fig.3. Cross sectional TEM images of single (Fe ion), dual (Fe+He ions) and triple (Fe+He+H ions) irradiations, shown between 1.0 μm (lower) and 1.6 μm (upper) in depth.](image)

![Fig.4. Depth distributions of Number density (left), average size of cavities (right) for dual (upper) and triple (down) irradiations.](image)
caused swelling around a depth range from 900 nm to 1.6 μm. Figure 4 shows the depth distributions of the number density (ND) of cavities (left), average size of cavities (right) for each ion irradiation of dual (upper) and triple (lower), estimated from high magnification TEM images. The data was obtained from a 100 nm step in width from surface to 1.9 μm in depth. The ND has a peak around 1.3 and 1.4 μm in depth for the cases of dual and triple ion irradiations, respectively. The peak ND for triple irradiation is about $1.0 \times 10^{22} \text{m}^{-2}$ which is less than half of that of dual irradiation, which was about $2.0 \times 10^{22} \text{m}^{-2}$. The average cavity size of the each 100 nm step in the dual irradiation condition was around 5 nm through the whole depth with cavity formation. However, the size in the triple irradiation condition increased up to be around 15 nm, which was significant from 1.4 to 1.6 μm in depth as compared with the dual irradiation one. The swelling behavior reflects both ND and cavity size. The sizes of cavities are comparable for both irradiation conditions but larger size cavities were observed in the triple irradiation condition as shown in Fig. 5. The maximum swelling of T91 was evaluated as 3.0 % at 1.2 μm in the dual irradiation condition at 500°C to 40 dpa. In the case of triple irradiation, the swelling was lower than that of dual irradiation at the depth from 0.9 to 1.3 μm. At a depth from 1.4 to 1.6 μm, however, the swelling increased distinctly for triple irradiation and showed maximum swelling of 6.9 % at 1.5 μm in depth. The mean swelling value after the dual and triple ion irradiations was 1.5 % and 2.0 %, respectively. The expected distributions of H and He atoms passing through the rotating Al energy degraders were statistically shown in Fig. 5. The maximum level of the concentration of H and He corresponded to 0.76 and 0.074 at%, respectively, in T91. In the case of dual irradiation the depth profile of swelling was reasonable with the He concentration distribution from the nucleation and growth of cavity point of view. It is known that the He atoms stabilize in the vacancy. The vacancy migration energy increased under displacement damage of α-Fe and F82H with He implantation [18]. He-vacancy complex and/or clusters could enhance the nucleation of cavity and as a result, the number density of cavities increased in the case of dual irradiation. It is not in the case of single irradiation because of no He atoms induced into the material. In the case of triple irradiation, the depth profile of swelling was shifted toward to deeper region as comparing with the expected H concentration. Diffusion of H atoms in steels is very fast at high temperature like a 500°C. After triple ion irradiation of F82H at 470°C the H atoms could not be detected anymore by nuclear resonance reaction [16]. The binding energy of H-vacancy and He-vacancy in α-Fe is about 0.6 and 2.0 eV, respectively [19, 20]. The hydrogen diffusivity is decreased due to the vacancy trap effect as comparing with mono-vacancy [19]. This indicates that H enhanced the irradiation swelling at the deeper depth region with higher displacement damage (vacancy defects) in this experiment. It is reported

![Fig.5. Depth distributions of displacement damage and swelling of dual (red) and triple (blue) irradiations. Depth profile of H and He were schematically shown by approximate lines for each concentration.](image)
that H atoms are trapped by He-vacancy complex and the vacancy migration energy increases due to He and H synergy [21, 22]. This synergy effect could also support that the cavity growth is enhanced at 1.5 μm in depth in the case of triple ion irradiation due to the H+He-vacancy complex with low mobility. Comparing the ND and cavity size following triple and dual irradiations, it was found that, under simultaneous triple ion beams (Fe+He+H), H atoms affected significantly on the swelling development process and the enhancement of cavity growth in the deeper region and the suppression of the growth in the medium depth region with changing the number density distributions of cavities might be caused by a fast diffusion of hydrogen atoms.

The FMS has high temperature strength, but, at relative low irradiation temperature around 300°C, radiation hardening/embrittlement happens mainly due to interstitial loops. In the case of ADS irradiation facility, the irradiation temperature of the beam window will be increased gradually under conditioning operation as increasing with the proton beam power. For this operation scenario, the temperature dependence of radiation damage like a swelling is very important and it has been studied in this experiment. Triple ion irradiations up to 10 dpa with gas ion implantation ratios of 15 appm He/dpa and 150 appm H/dpa formed some cavities for 350, 450 and 550°C for T91 as shown in Fig. 6. The cavities with mean size of 4 nm dispersed sparsely in the case of the irradiation at 350°C, the mean number density was 1.4×10²⁰ m⁻³ and the maximum swelling was 0.14 % at 600 nm in depth. In the case of 550°C, the mean size and number density of the cavities were increased to be 6 nm and 2.5×10²¹ m⁻³, respectively, and the maximum swelling was 0.33 % at 800 nm in depth. In the case of triple ion irradiation at 450°C, the mean size of the cavities grew obviously up to 10 nm, the number density was 1.6×10²¹ m⁻³ and the swelling showed the maximum value of 1.65 % at 600 nm in depth. The peak swelling temperature could be quantitatively explained from the view point of temperature. At the irradiation temperature of 350°C vacancies caused by ion irradiation can’t migrate enough to grow the many cavities but interstitials can diffuse easily and then dislocation loops dominants mainly around this relative low temperature. On the other hand, at 550°C the vacancies can migrate, nucleate and grow the cavities. Some vacancies also
partially recombine with the interstitials and also disappear at sink sites like a grain boundary, which means that the suppression of the cavity growth happened and shows in the middle value of swelling at 550°C in this experiment. Under the irradiation at 450°C both interstitial loops and cavities are formed as observed by TEM, which indicates that the opportunity of the recombination between an interstitial atom and a vacancy decreases by forming loops and cavities. Formation of the loops and cavities after irradiation support the hardening and swelling behavior as shown later in Fig. 7 and in Fig. 6.

Irradiation hardening occurred simultaneously with the maximum swelling for the irradiation at 450°C. The irradiation hardening decreased as the irradiation temperature increased, as shown in Fig. 7. The normalized hardness means irradiation hardening, which is calculated by dividing the hardness after irradiation by that of before. The displaced interstitials make interstitial loops, which cause hardening. On the counterpart, the supersaturated vacancies combined with He and/or H atoms to nucleate and grow cavities and these cavities continued to grow. Such a drastic decrease in the swelling in the temperature region around 500°C has been reported for F82H in Ref. [4]. Such temperature-dependent swelling could be a common phenomenon for FMS like a F82H and T91. Optimization of heat treatments is one of the promising techniques to suppress radiation degradation such as radiation hardening [23]. FMS steels have a complex microstructure, like the prior austenitic grain boundaries, lath boundaries, packets, blocks, carbides and strain dislocations, which size and density depend on the normalizing and tempering conditions. On the other hand, it was reported that work hardening, which increased dislocation density, could suppress the swelling [17]. The design of ADS non-critical core has not been fixed yet, but in the feasibility study of ADS, main components refer the design of fast reactors [2]. For the cladding tubes in a fast reactor the allowable maximum diametral strain of 7% [24] includes both strains by the swelling and creep. Assuming that the swelling shares half of the strain (3.5%), the limit of swelling for the cladding is about 10% in volume. In the case of swelling rate of triple irradiation at 450°C being 1.65% in this study, 10/1.65 multiplied by 10 equals to 60 dpa, which might be a damage limit by considering only the case of swelling caused by displacement damage, helium and hydrogen gas accumulations. It is noted that cladding materials will not be actually irradiated by so much hydrogen in ADS, the volume strain due to the swelling is isotropic and the swelling rate could be slower than this experiment [25]. Then, this swelling limit value of 60 dpa might be overestimated. It is well known that neutron irradiation caused embrittlement, as a DBTT (Ductile Brittle Transition Temperature) shift for the FMS. The DBTT after irradiation needs to be managed below the lower
limit of the LBE coolant temperature about 230°C [2]. Empirical correlation between Vickers hardness (HV) and micro-hardness (HM) for the irradiated FMS was reported by Ando, et al. [26] as follows: \( \sigma_y = 60 \times H_v \), where, \( H_v \) is in kg/mm\(^2\) and \( H_m \) in GPa. Also, the correlation between tensile strength (\( \sigma_y \)) and Vickers hardness was reported as follows: \( \sigma_y = 60 \times H_v \times (0.1)^{0.05} \), where \( \sigma_y \) is in MPa and \( H_v \) is in kg/mm\(^2\).

In the case of triple ion irradiation at 450°C the micro-hardness was 3.72 GPa, as shown in Fig. 7. The \( \sigma_y \) is calculated to be 656 MPa by using above correlations. The \( \sigma_y \) of non-irradiated T91 at RT is 506 MPa [27] and the \( \Delta \sigma_y \) is 150 MPa. From empirical relationship between DBTT shift and \( \Delta \sigma_y \) after irradiation in HFIR for FMS [28], the DBTT shift was +50°C and the DBTT after 10 dpa irradiation was estimated to be below RT. Even after irradiation at 350°C the DBTT of 25°C was enough lower than 230°C in the case of ADS irradiation conditions with displacement damage, helium and hydrogen gas accumulations. It is noted that if one compare the radiation-damage behavior between ion and neutron irradiations the results always include some cares due to two or three orders difference of the damage rate. That is the reason why the ADS material irradiation experimental facility [6] is necessary for confirming and supporting the irradiation data to design the ADS components.

### 3.2 LMC behavior after irradiation

In the T91 steel after soaking in LBE, the cross sectional SEM image taken from triple irradiated region showed the thicker oxide layer than that of the non-irradiated surface at low oxygen concentration of the order of 10\(^{-9}\) wt%. Triple ion irradiation up to 8 dpa at the specimen surface and the gas implantation ratios of 15 appm He/dpa and 150 appm H/dpa around 1 \( \mu \)m in depth was conducted at 450°C followed by corrosion test at 450°C for 381 hours. Figure 8 shows the cross-sectional SEM image around the boundary between irradiated and non-irradiated (masked) area on the surface of the specimen. The EDS line spectra in the each area are also shown in this Figure. An oxide layer with a few hundred nm in thickness, observed as a very thin white contrast, was formed on the surface of the non-irradiated region. On the other hand, a distinct oxide layer with a few \( \mu \)m in thickness, which was ten times thicker than that of non-irradiated, covered on the surface of the irradiated area. The breakage of the oxide layer was caused by polishing in the irradiated region. It was found by

![Fig.8. Cross-sectional SEM images and EDS line spectra. Specimen was triply irradiated up to 8 dpa at surface at 450°C. Corrosion test was conducted under low oxygen concentration around 10\(^{-9}\) wt%.](image-url)
XRD analysis that the oxide layers of the non-irradiated and irradiated areas composed with both Fe$_3$O$_4$ (Magnetite) and FeCr$_2$O$_4$ (Spinel). It is known that in the case of corrosion in LBE with satisfying enough high oxygen concentration with a range of $10^{-4}$ to $10^{-6}$ wt% and/or longer time typically over than 1000 hours, so-called duplex oxide layer forms on the steel surface [9, 28]. The outer layer is Fe$_3$O$_4$ and inner layer is FeCr$_2$O$_4$ in this duplex layers. In this experiment the duplex layer could not be observed in the SEM images and EDS line spectrum of the irradiated area because the oxygen concentration was low and the corrosion time was not enough to grow to be duplex layer, nevertheless, triple ion irradiations could enhance definitely the oxidation reaction by using the oxygen effectively, which was induced into the LBE only due to 10 % duration of relatively high oxygen concentration at the beginning of corrosion test, which was shown in Fig. 2 (a). In the case of T91 steel after soaking in LBE under saturated oxygen concentration at $2.4 \times 10^4$ wt%, the surface of non-irradiated and irradiated region consisted of the duplex oxide layers. Figure 9 shows the typical cross-sectional SEM images for non-irradiated and irradiated area on the surface of the specimen, followed by corrosion test at 450°C during 330 hours. The triple ion irradiation was conducted up to 8 dpa at the specimen surface and the gas implantation ratios were 15 appm He/dpa and 150 appm H/dpa around 1 μm in depth. The boundary between outer and inner layers is clearly observed in the case of non-irradiated area. In the case of irradiated area, however, the boundary is not so clear but it can be somewhat distinguishable. Figure 9 was taken from one specimen and the both areas were polished side by side by same condition. Even both areas passed same preparing process the morphology of outer oxide layer was different each other. The outer layer of non-irradiated area looks dense and some long cracks passing through the layer, but the irradiated one looks coarse and many cracks appear. As denoting in previous paragraph, because of the high oxygen concentration in this corrosion condition, the outer layer was Fe$_3$O$_4$ and inner layer was FeCr$_2$O$_4$ in the duplex layer. The oxide layers were confirmed by the XRD and EDS measurements. The mutual process of inward diffusion of oxygen from LBE side and outward diffusion of iron from steel matrix governs the oxide formation around the boundary between the steel surface and LBE. It is supposed that the original surface is placed between the outer and inner layers. This indicates that the inner layer of the irradiated region includes radiation damage. The mean thicknesses and standard deviations of the outer and inner layers of non-irradiated and irradiated areas were shown in Table 2. The total thickness was also measured from the each image. The thickness of the inner layer for the irradiated

![Fig.9. Cross-sectional SEM images of non-irradiated and irradiated area. Specimen was triply irradiated up to 8 dpa at 450°C. Corrosion test was conducted under saturated oxygen concentration around $10^4$ wt%.

Table 2. Thickness of duplex layers (μm).

|       | Non-irrad. | Irrad.  |
|-------|------------|---------|
| Outer | 2.55 ± 0.15| 1.93 ± 0.54|
| Inner | 1.21 ± 0.32| 1.31 ± 0.38|
| Total | 3.83 ± 0.40| 3.65 ± 0.39|

The average thickness was measured from 40-50 points with 1.5 μm distance.
region doesn’t change so much as comparing with non-irradiated one. However, the thickness of the outer layer for the irradiated area is about 600 nm thinner than that for the non-irradiated one. As shown in Fig. 8, the oxide formation was enhanced by the triple ion irradiation even at low oxygen concentration in LBE through the radiation defects. In the case of non-irradiated region the outer oxide layer can grow in LBE with high oxygen concentration under thermal equilibrium state. The thermal equilibrium state is also applicable to the irradiated region because oxidation reaction causes after the ion irradiation. However, the number of Fe atoms diffusing outward might increase by using site change with the vacancies, which might be trapped by some impurities, strain field, etc., induced by ion irradiation, more than Fe self-diffusion under the thermal activity process. Activation energy of the Fe self-diffusion in α-Fe is 2.9 eV, where the vacancy formation energy (E_{vf}) and migration energy (E_{vm}) are 1.6 and 1.3 eV, respectively [30]. Diffusion coefficient, D is calculated by D=D_{0} \exp (-E_{vf}+E_{vm})/kT, where, D_{0} is 8.0 \times 10^{-5} m^2/s, k: 8.62 \times 10^{-5} eV/k and T:723 k, respectively. The thermal diffusion length, L_{d}, is denoted by L_{d}=(6D_{0}t)^{1/2}, and the L_{d} of Fe is calculated to be 1.4 nm under the corrosion test at 450°C for 330 hours. The Fe self-diffusion doesn’t affect the oxide formation in the surface. After ion irradiation, assuming all vacancies exist even at RT, when the E_{vf} =0, which means the neighbor of the diffusive atom is vacancy, the diffusion coefficient shows the maximum value and the L_{d} is 580 μm. The L_{d} is indeed shorter than this maximum value because of the recombination with the interstitial and the disappearance to the sink site. As discussed in previous section, the vacancy migration energy increases due to He and H synergy. This synergy effect could also support that the vacancy clusters, He-V and/or He-V-H complexes could emit some vacancies at the corrosion temperature and Fe diffusion could be enhanced in the irradiated region. On the other hand, oxygen atoms diffuse inward from the surface as interstitial atoms. The migration energy of interstitial atom, E_{im} is 0.89 eV [30]. D=D_{0} \exp (-E_{im})/kT, where, D_{0} is 1.79 \times 10^{-7} m^2/s, k: 8.62 \times 10^{-5} eV/k and T:723 k, respectively. The oxygen diffusion length, L_{d}=(6D_{0}t)^{1/2}, is calculated to be 910 μm. The oxygen can diffuse sufficiently inward to the material in this corrosion experiment in LBE. This enhances the oxidation reaction between O and Fe and the higher oxidation rate could cause a spallation of oxide layers from the surface. This also could reduce the thickness of outer layer for the irradiated region as shown in Table 2. It is supported that the surface morphology of irradiated area shows rougher than that of non-irradiated one as shown in Fig. 9. From these rough estimations two reasons why the corrosion rate increases in the case of triple ion irradiations are considered; (1) enhancement of Fe diffusion caused by reducing activation energy of Fe atoms due to helium-vacancy complexes and vacancy clusters after the ion irradiation and (2) enhancement of O interstitial diffusion induced by radiation damage.

The 1000 hour corrosion test in LBE after ion irradiation was conducted at low oxygen concentration around 10^{-8} and 10^{-9}.

---

*Fig. 10. SEM and EDS mapping images of non-irradiated region after 1000 hour corrosion test.*
wt%. The SEM images and EDS mapping are shown in Figs. 10 and 11 for the non-irradiated and irradiated regions, respectively. The single ion irradiation was conducted by 10 MeV-Fe\(^{3+}\) at 450°C to induce only the displacement damage without gas atoms. The cross sectional SEM images of the ion irradiated region showed the thinner surface oxide layer as comparing with the non-irradiated one. The outflow of Fe into the LBE adherent to the steel surface was observed on the irradiated region. The oxide layer, which included Fe and Cr, formed with the thickness about 5 \(\mu\)m in the case of non-irradiated region due to relatively high concentration oxygen under first 15 \% ratio of the total corrosion time in 1000 hours, which was shown in Fig. 2 (b). In the case of irradiated region, however, the oxide thickness decreased to be about 2 \(\mu\)m and some Fe oxides were observed in the LBE as shown in Fig.11. The XRD analysis showed that both the oxide layers of the non-irradiated and irradiated region composed with both Fe\(_2\)O\(_4\) and FeCr\(_2\)O\(_4\). It’s not the duplex layer because of the low oxygen concentration. The Fe oxides were embedded in the surface LBE layer of the irradiated region shown as some dark contrasts in the bright contrast of LBE in the SEM image of Figs.11 and 12. Figure 12 shows the SEM image of irradiated area, which corresponds to Fig.11. In the right side of the image shows thicker oxide layer with around 3 \(\mu\)m in thickness. The original surface is not clear for this long time corrosion test under low oxygen concentration. If the double arrow shows the tentative irradiation damage zone with 2 \(\mu\)m in depth referring only the displacement damage as shown in Fig.5, some area remains the oxide layer but the other area doesn’t remain. The Fe\(_2\)O\(_4\) layer could be dissolved by the reduction reaction under the critical low oxygen concentration of around 10\(^9\) wt\%. The single ion irradiation at 450°C doesn’t form the cavities from the extrapolation of the swelling behavior already shown in Sec.3.1, which suggests that after the irradiation the vacancy doesn’t remain so much because no trapping effects due to He and/or H gases implanted. Even if vacancies remain somewhat and enhance the Fe diffusion and oxidation at the beginning of the corrosion test, the following long time reduction reaction attacks the oxide layer under the original surface with displacement damage (radiation defects). The ADS irradiation conditions with displacement damage, He and H generations could be appropriate for the FMS facing LMC, especially for the case of decreasing the oxygen concentration when some troubles for the oxygen control system happened in the system. It is suggested that radiation induced diffusion under irradiation will enhance the oxidation much more than that after the irradiation like in this study.
3. Conclusion

The swelling and the LMC behavior of T91 steels after ion irradiation, in the cases of self-ion irradiation and simultaneous irradiation with He and H atoms, were investigated. In the case of single ion irradiation (only displacement damage), no cavities were observed, but in the cases of dual and triple ion irradiations, many cavities appeared and caused swelling. It was concluded that helium and/or hydrogen enhanced the swelling induced by the simultaneous irradiation case and the peak swelling behavior appeared at an irradiation temperature around 450°C. The triple ion irradiation influence on LMC of T91 steels was firstly estimated for the specimen irradiated at 450°C. After the corrosion test at 450°C in the LBE with low oxygen concentration, the surface of the irradiated area was covered by the oxide layer even though the non-irradiated area didn’t show the enough oxide formation. From this study, it is found that the irradiation enhances the oxide layer formation through the irradiation defects in T91 steels. The oxide layer might be partially reduced and dissolved into the LBE by reduction reaction following long time corrosion at lower oxygen concentration.

Acknowledgment

The authors thank to Drs. Y. Abe and M. Itakura in JAEA for their useful discussions and great thanks to Dr. E. Wakai and Prof. S. Ukai in JAEA for their advices on preparing this manuscript. These ion irradiation works were done under the Shared Use Program of QST Facilities.

References

[1] K. Tsujimoto, H. Oigawa, K. Kikuchi, Y. Kurata, M. Mizumoto, T. Sasa, S. Saito, K. Nishihara, M. Umeno and H. Takei, Nucl. Tech., 161, 315, (2008).
[2] K. Tsujimoto, K. Nishihara, H. Takei, T. Sugawara, Y. Kurata, S. Saito, H. Obayashi, T. Sasa, K. Kikuchi, M. Tzuka, and H. Oigawa, JAEA-Research 2010-012.
[3] M. Ando, T. Nozawa, T. Hirose, H. Tanigawa, E. Wakai, R. E. Stoller and J. Myers, Fusion Science and Technology, 68, 648, (2015).
[4] E. Wakai, S. Matsukawa, T. Yamamoto, Y. Kato, F. Takada, M. Sugimoto and S. Jitsukawa, Materials Transactions, 45, 2641, (2004).
[5] Z. Tong, Y. Dai, J. Nucl. Mater., 398, 43, (2010).
[6] T. Sasa and H. Oigawa, Plasma Fusion Res., 9, 113, (2014).
[7] G Müller, A Heinzl, G Schumacher, A Weisenburger, J. Nucl. Mater., 321, 256,(2003).
[8] G Müller, G Schumacher, F Zimmermann, J. Nucl. Mater., 278, 85, (2000).
[9] V. Tsisar, C. Schroer, O. Wedemeyer, A. Skrypnik, J. Konys, J. Nucl. Mater., 494, 422, (2017).
[10] C. Schroer, O. Wedemeyer, A. Skrypnik, J. Novotny and J. Konys, J. Nucl. Mater., 431, 105, (2012).
[11] E. Stergar, S. G. Eremin, S. Gavrilov, M. Lambrecht, O. Makarov and V. Iakovlev, J. Nucl. Mater., 473, 28, (2016).
[12] A.J. Magielsen, M. Jong, T. Bakker, N.V. Luzginova, R.K. Mutnuru, D.J. Ketema and A.V. Fedorov, J. Nucl. Mater., 415, 311, (2011).
[13] J. F. Ziegler "SRIM-2003". Nucl. Instr. Meth. B, 219, (2004).
[14] H. Iwamoto, K. Nishihara, Y. Iwamoto, S. Hashimoto, J. Nucl. Sci. Technol., 53, 1585, (2016).
[15] T. Sugawara and K. Yamaguchi, JAEA-Technology 2015-022.
[16] E. Wakai, T. Sawai, K. Furuya, A. Naito, T. Aruga, K. Kikuchi, S. Yamashita, S. Ohnuki, S.
Yamamoto, H. Naramoto, and S. Jitsukawa, J. Nucl. Mater. 307-311, 278, (2002).
[17] E. Wakai, K. Kikuchi, S. Yamashita, T. Aruga, M. Ando, H. Tanigawa, T. Taguchi, T. Sawai, K. Oka, and S. Ohnuki, J. Nucl. Mater. 318, 267, (2003).
[18] N. Hashimoto, S. Sakuraya, J. Tanimoto and S. Ohnuki, J. Nucl. Mater. 445, 224, (2014).
[19] D. Zhu and T. Oda, J. Nucl. Mater. 469, 237, (2016).
[20] Y. Liu, Y. Yu and Z. Dai, J. Nucl. Mater. 456, 162, (2015).
[21] J. Shi and N. Hashimoto, Nucl. Mater. Energy, 16, 212, (2018).
[22] P. Liu, Q. Zhan, W. Han, X. Yi, S. Ohnuki and F. Wan, J. Alloys. Comp. 788, 446, (2019).
[23] N. Okubo, M.A. Sokolov, H. Tanigawa, T. Hirose, S. Jitsukawa, T. Sawai, G. Odette and R. Stoller, J. Nucl. Mater. 417, 112, (2011).
[24] T. Uwaba, M. Sogame, M. Ito, T. Mizuno, T. Donomae and K. Katsuyama, J. Nucl. Sci. Technol., 47, 712, (2010).
[25] IAEA Nuclear Energy Series, No. NF-T-4.2, Structural Materials for Liquid Metal Cooled Fast Reactor Fuel Assemblies — Operational Behaviour, 2012
[26] M. Ando, E. Wakai, H. Tanigawa and Y. Kawasaki, J. Japan Inst. Metals, 72, 785, (2008).
[27] Metallic Material Database, Kinzoku, produced by NIMS.
[28] M.A. Sokolov a, H. Tanigawa, G.R. Odette, K. Shiba and R.L. Klueh, J. Nucl. Mater. 367, 68, (2007).
[29] LBE HANDBOOK, NEA No. 7268, 2015, published by OECD/NEA
[30] Y. Watanabe, K. Morishita, T. Nakasuji, M. Ando and H. Tanigawa, Nucl. Instr. Meth. Phys. Res. B 352, 115, (2015).